

UNIVERSIDADE DE SÃO PAULO  
FACULDADE DE ZOOTECNIA E ENGENHARIA DE ALIMENTOS

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**Citrus essential oil fractionation using ethanol with different water contents as solvents: Phase equilibrium, physical properties and continuous equipment extraction**

**“Fracionamento de óleos essenciais cítricos utilizando etanol com diferentes níveis de hidratação como solventes: Equilíbrio de fases, propriedades físicas e extração em equipamento contínuo”**

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“The most beautiful experience we can have is the mysterious. It is the fundamental emotion that stands at the cradle of true art and true science”

Albert Einstein

“A thinker sees his own actions as experiments and questions as attempts to find out something. Success and failure are for him answers above all”

Friedrich Nietzsche

## ABSTRACT

GONÇALVES, D. **Citrus essential oil fractionation using ethanol with different water contents as solvents: phase equilibrium, physical properties and continuous equipment extraction.** 2017. 239 p. Ph.D. Thesis – Faculty of Animal Science and Food Engineering, University of Sao Paulo, Pirassununga/SP, Brazil, 2017.

Essential oils are featured commodities in the global market due their many applications in food and chemical industries, in different medicine areas, and as antibacterial, antifungal, and antioxidant agent. One of the phenomena accountable for the loss of essential oils quality may be associated with the degradation of terpene hydrocarbons by oxidation when exposed to air, light or heat, causing disagreeable odors. The procedure of terpenes content reducing, known as deterpenation, can be performed by diverse techniques, among which the liquid–liquid extraction can be highlighted since this process can be operated without the use of heating and pressure changes, causing low impact on the essential oil sensory qualities and low energy consumption.

This research was focused on the fractionation process of citrus essential oils, by liquid–liquid extraction, using ethanol/water mixtures as solvents. Experimental liquid–liquid equilibrium data of model and real citrus systems were obtained. The aroma profile of the crude citrus essential oils (orange - *Citrus sinensis* and lime - *Citrus aurantifolia*) and the phases from the liquid–liquid equilibrium was also evaluated. Moreover, the crude citrus essential oils were fractionated in a continuous operation equipment (perforated rotating disc contactor, PRDC). It was verified that the water has an important influence over the fractionation performance, but not over the aroma profile of the phases. The experimental data from the model systems (citrus essential oil model mixture + ethanol + water) were used to adjust parameters of empirical and thermodynamic models, which provided satisfactory results on the calculation of physical property values and compositions of the phases from the real systems (crude citrus essential oil + ethanol + water). The fractionation of citrus essential oils by liquid–liquid extraction technology was technically feasible and can be accomplished into continuous apparatus such as PRDC column. The solvents employed provided extract phases enriched in oxygenated compounds.

Keywords: Liquid–Liquid Equilibrium – Deterpenation – Solvent Extraction – Modelling – Aroma Profile

## RESUMO

GONÇALVES, D. **Fracionamento de óleos essenciais cítricos utilizando etanol com diferentes níveis de hidratação como solventes: Equilíbrio de fases, propriedades físicas e extração em equipamento contínuo.** 2017. 239 p. Tese de Doutorado – Faculdade de Zootecnia e Engenharia de Alimentos, Universidade de São Paulo, Pirassununga/SP, Brasil, 2017.

Óleos essenciais são importantes produtos comercializados mundialmente devido às suas diversas aplicações em indústrias alimentícias e químicas, em diferentes áreas da medicina, e como agentes antibacteriano, antifúngico e antioxidante. Um dos fenômenos responsáveis pela sua perda de qualidade pode estar associado à degradação dos hidrocarbonetos terpênicos por oxidação, quando estes são expostos ao ar, luz ou calor, ocasionando odor desagradável. O procedimento para redução do teor de terpenos no óleo essencial, conhecido como desterpenação, pode ser realizado por diferentes técnicas, entre as quais a extração líquido-líquido se destaca uma vez que pode ser conduzida sem o emprego de calor e mudanças na pressão, o que atenua o impacto nas qualidades sensoriais e demanda menor gasto energético.

Este estudo se concentrou no processo de fracionamento de óleos essenciais cítricos, pela técnica de extração líquido-líquido, empregando misturas de etanol e água como solventes. Foram obtidos dados de equilíbrio líquido-líquido de sistemas cítricos modelo e reais. O perfil de aroma dos óleos essenciais brutos (laranja - *Citrus sinensis* e lima ácida *Citrus latifolia*) e das fases provenientes do equilíbrio líquido-líquido também foram avaliados. Além disso, os óleos essenciais brutos foram submetidos ao processo de fracionamento em equipamento de operação contínua (coluna de discos rotativos perfurados, PRDC). Verificou-se que a água possui uma importante influência sobre o desempenho do processo de fracionamento, mas não afetou o aroma das fases. Os dados experimentais dos sistemas modelo (mistura modelo de óleo essencial cítrico + etanol + água) foram utilizados para o ajuste de parâmetros de modelos empíricos e termodinâmicos, os quais apresentaram bons resultados no cálculo de valores de propriedades físicas e da composição das fases oriundas dos sistemas reais (óleo essencial cítrico bruto + etanol + água). O fracionamento de óleos essenciais cítricos pela tecnologia de extração líquido-líquido mostrou-se tecnicamente viável e pode ser conduzido em equipamentos contínuos como a coluna de extração PRDC. Os solventes empregados permitiram a obtenção de fases extrato enriquecidas com compostos oxigenados.

Palavras-chave: Equilíbrio Líquido-líquido – Desterpenação – Extração por Solvente – Modelagem – Perfil de Aroma

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## 1. PRESENTATION

This PhD. Thesis had as main hypothesis that citrus essential oil can be fractionated by the solvent extraction technique, using ethanol/water mixtures as solvents. The orange (*Citrus sinensis* L. Osbeck) and acid lime (*Citrus latifolia* Tanaka) peel oils were the focus of this study. For that, the evaluation of the process was based on four pillars: (i) obtainment of liquid–liquid equilibrium data of model and real systems; (ii) study of the physical properties of the phases from the liquid-liquid equilibrium; (iii) estimation of the aroma profile of crude essential oils and their phases from the liquid–liquid equilibrium; (iv) fractionation of real systems in a continuous equipment (perforated rotating disc contactor). The themes are discussed in the chapters of this document, which correspond to the original scientific articles already published or submitted to scientific journals. The items (i), (ii), and (iv) were developed at the Laboratory of Separation Engineering (LES), Faculty of Animal Science and Food Engineering (FZEA), University of São Paulo, Pirassununga/SP, Brazil, with Professor Dr. Christianne E. da C. Rodrigues as advisor and the collaboration of Dr. Cintia B. Gonçalves and Dr. Alessandra L. de Oliveira. The item (iii) was carried out at the Laboratory of Perfumery Engineering, Faculty of Engineering of the University of Porto (FEUP), Porto, Portugal, under supervision of the postdoctoral researcher Dr. Patrícia Costa (Portugal) and Professor Dr. Alírio E. Rodrigues (Portugal), responsible for the laboratory, and advised by Professor Dr. Christianne E. C. Rodrigues (Brazil).

In Chapter I, the fractionation of limonene and linalool mixtures (model systems) and crude orange essential oil (real systems), using ethanol and water mixtures as solvents, is discussed. The evaluation of the process was carried out by the determination of liquid–liquid equilibrium data at 298.2 K, adjustment of binary interaction parameters of the NRTL and UNIQUAC thermodynamic models, and their use to calculate the composition of the phases from the real systems. This chapter corresponds to the scientific article published in *Fluid Phase Equilibria* journal, and its use were permitted by Elsevier to make a part of this document. The liquid–liquid equilibrium data of the systems composed of limonene + linalool + ethanol + water, at 298.2 K were obtained during the master's degree. The adjustment of the binary parameters, obtainment of liquid–liquid equilibrium data of the real system, writing, review and publishing of the article were done during the doctorate course.

Chapter II corresponds to the evaluation of the aroma profile of the crude orange essential oil and the phases from the liquid–liquid equilibrium of systems composed of crude orange essential oil + ethanol + water, at 298.2 K. This study was carried out at the Laboratory of Perfumery Engineering, Portugal. This chapter is the original manuscript accepted for publication in *The Journal of Chemical Thermodynamics*. All publishing rights are of Elsevier.

Chapter III presents the fractionation of limonene and linalool mixtures (model system) and crude orange essential oil in a continuous equipment (Perforated rotating disc contactor, PRDC). The best operational conditions were determined using the model mixture and applied for the fractionation of the crude essential oil. This chapter corresponds to the scientific article published in the *Separation and Purification Technology* journal, and was added to this document with permission of Elsevier. The assays were done during the master's degree, and the process performance of the PRDC can be also verified in Gonçalves (2013)<sup>1</sup>. The better data interpretation, the calculation of two complex indices (overall volumetric mass transfer coefficient and mass transfer units), writing, review and data publishing were done during the doctorate course.

In Chapter IV, the crude acid lime essential oil was submitted to the fractionation process using ethanol and water as solvents. The aroma profile of the phases from the liquid–liquid equilibrium of systems composed of crude acid lime essential oil + ethanol + water, at 298.2 K, was evaluated. The compositions of the phases from the liquid–liquid equilibrium were calculated using the binary parameters of the NRTL model from the literature. This work was published in *The Journal of Chemical Thermodynamics*, and is a part of this document with permission of Elsevier.

In Chapter V, several liquid–liquid equilibrium data of systems composed of crude acid lime essential oil + ethanol + water, at 298.2 K are shown. The compositions of the phases were calculated using binary parameters of the NRTL model from the literature. The performance of the PRDC on the fractionation of crude acid lime essential oil, using ethanol

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<sup>1</sup> GONÇALVES, D. *Estudo do Processo de Desterpenação de Óleos Essenciais Cítricos: Dados de Equilíbrio Líquido-líquido e Extração em Coluna de Discos Rotativos Perfurados*. Dissertation Thesis, Food Engineering Department, University of São Paulo, Pirassununga/SP, Brazil, 2013.

and water as solvents, was also evaluated. This chapter is in article format which will be submitted to a scientific journal for further publication.

In Chapter VI, liquid–liquid equilibrium data of model systems composed of limonene + linalool + ethanol + water, and  $\beta$ -pinene + limonene +  $\gamma$ -terpinene + ethanol + water, and real systems composed of crude orange or acid lime essential oils + ethanol + water, at 298.2 K are presented. In this chapter, the physical properties of the phases from the equilibrium are discussed, such as density, viscosity, and interfacial tension. The model system data were used to adjust parameters of empirical models, which were employed to calculate the properties of the phases from the real systems. As the Chapter VI, this chapter is in article format which will be submitted to a scientific journal for further publication.

## 2. INTRODUCTION

### 2.1. Essential oils trading data

Brazil has an important participation on the international trading. The chief Brazil's exports are soybeans, iron ore, crude petroleum, raw sugar, poultry meat, soybean meal, and frozen bovine. It is the main exporter of some commodities from the agribusiness, such as coffee, orange juice (concentrated or not), orange essential oil, soybean oil, and others (OEC, 2017; UNCOMTRADE, 2017). In 2015, almost 18% of all Brazil's exportation was from the agribusiness. In this year, the country was responsible for 36% of orange essential oil's exportation, being the main exporter of this raw material. Relating to the lemon essential oil, Brazil was responsible for only 0,94% of world's exports, being Argentina the main exporter of this raw material (38% in 2015) (OEC, 2017). The Brazil's participation in the essential oil market is better demonstrated in Table 1, where is possible to verify that in 2016 the country was the main exporter of essential oils, resinoids and terpenic byproducts, mainly due to its leadership in the orange essential oil trade for a long time.

**Table 1:** Brazil's essential oils exports trading data\*

Product	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016
<i>Essential oils resinoids terpenic byproducts</i>										
Netweight (tons)	68681	72534	68681	70217	59443	66829	68915	56348	55916	52655
Trade Value (US\$ mi)	126.4	155.4	126.4	165.9	263.4	244.9	202.9	228.6	256.9	339.0
World's ranking	1	1	1	1	1	1	1	1	2	1
<i>Orange Essential Oil</i>										
Netweight (tons)	31753	30079	28409	28834	24148	30389	30926	25460	25614	27780
Trade Value (US\$ mi)	70.8	70.9	55.9	74.6	111.6	124.2	103.6	111.7	133.4	194.2
World's ranking	1	1	1	1	1	1	1	1	1	1
<i>Lemon Essential Oil</i>										
Netweight (tons)	400	264	265	262	18	157	146	328	209	400
Trade Value (US\$ mi)	6.0	6.2	6.4	7.7	6.0	4.1	3.9	7.9	5.3	8.4
World's ranking	9	13	11	12	13	14	15	15	13	9

\* Compiled data from UNComtrade (2017).

Traditionally, the foremost use of citrus essential oils is to reincorporate the aroma in citrus juices, which the sensorial qualities depend on each consumer (BAŞER and BUCHBAUER, 2010). In 2015, the most important importers of orange essential oil from Brazil were the USA (49%), Germany (13%), Switzerland (11%), Argentina (9.6%), Paraguay (6.8%), Italy (2.9%), Spain (2.5%) and France (2.3%), which are significant producers and consumers of citrus juice (OEC, 2017).

The main exporters of essential oils in the world in 2016 are presented in Table 2, where it is possible to verify that Brazil is the main exporter of essential oils, followed by China. Relating to lemon essential oil, Brazil was ranked as the 9<sup>th</sup> main exporter, and the 10<sup>th</sup> main exporter of essential oils extracted from other citrus fruits (not oranges, lemon, limens or bergamot). Although Brazil is ranked as an important essential oil exporter, its trade value is lower than the one of other countries which exported less quantity than Brazil, such as the USA, India, and France. This fact can be due to the raw material quality, mainly in terms of oxygenated compounds concentration in the mixture, which is an important factor to establish its trading value. In this context, we can point that is interesting and required a technique that makes possible the improvement of Brazil's essential oils, in terms of higher oxygenated compounds amount in relation to terpenes. From this gap, this research becomes significant.

**Table 2:** World's trade data in essential oils exports, in 2016.<sup>a</sup>

Ranking	Essential oils, resinoids, terpenic byproducts			Orange Essential Oil			Lemon Essential Oil			Other Citrus Essential Oils <sup>b</sup>		
	Reporter	Netweight (tons)	Trade Value (US\$ million)	Reporter	Netweight (tons)	Trade Value (US\$ million)	Reporter	Netweight (tons)	Trade Value (US\$ million)	Reporter	Netweight (tons)	Trade Value (US\$ million)
1	<b>Brazil</b>	<b>339048</b>	<b>52.66</b>	<b>Brazil</b>	<b>194208</b>	<b>27.78</b>	Argentina	186205	5.63	U.S.A.	80072	2.41
2	China	423524	32.43	U.S.A.	88032	9.13	China	35389	4.43	Mexico	74757	2.19
3	Indonesia	166380	30.77	Mexico	34795	5.28	Italy	47734	2.13	China	11503	1.36
4	U.S.A.	634488	28.97	Belgium	8321	3.72	U.S.A.	53187	1.83	Italy	59695	1.04
5	India	607726	23.28	Germany	36744	2.81	Mexico	26059	0.96	United Kingdom	39693	0.99
6	Mexico	144926	8.77	Costa Rica	10871	2.55	United Kingdom	25770	0.07	South Africa	8782	0.86
7	United Kingdom	221361	7.72	Belize	3097	1.80	Peru	18848	0.59	Belize	1175	0.53
8	Germany	191524	7.60	Canada	18090	1.78	Germany	22203	0.05	Germany	21970	0.37
9	Argentina	196376	6.80	United Kingdom	19859	1.13	<b>Brazil</b>	<b>8432</b>	<b>0.40</b>	India	6099	0.32
10	France	396745	6.43	Italy	10891	0.93	Canada	9036	0.35	<b>Brazil</b>	<b>13269</b>	<b>0.29</b>
11	Spain	124928	5.23	Spain	8447	0.83	Dominican Rep.	215	0.03	Israel	7789	0.25
12	Italy	137698	4.82	China	5860	0.72	Spain	10739	0.33	Malaysia	942	0.24
13	Belgium	50580	4.66	South Africa	6142	0.70	South Africa	6907	0.00	Spain	4773	0.20
14	Canada	68117	3.50	Argentina	4499	0.56	France	8818	0.22	Canada	5425	0.16
15	Costa Rica	11341	2.68	Ireland	6296	0.41	Ireland	6081	0.14	France	7658	0.14

<sup>a</sup> Compiled data from UNComtrade (2017).<sup>b</sup> Citrus essential oils not from oranges, lemons/limes, and bergamot.

## 2.2. Chemical characterization of citrus essential oils

Citrus essential oils are traditionally extracted from the peels of citrus fruits, such as oranges, lemons, limes, bergamots, mandarins, and grapefruits. They are composed of a complex mixture of volatile hydrocarbons, alcohols, aldehydes, esters, ketones, and ethers, which can constitute more than 95% of the oil, by weight, and non-volatile compounds, as waxes, flavonoids, carotenoids, acids, and coumarins, in smaller fraction (from 1 to 10%, by weight) (CHÁFER et al., 2004; CHIYODA et al., 2011; GIRONI; MASCHIETTI, 2008; LAGO et al., 2012, 2014; MARTINS et al., 2013; MASSON et al., 2016; MEHL et al., 2014; RAEISSI; PETERS, 2005a; RUSSO et al., 2015). Citrus essential oils are important raw materials incorporated in several products, such as in beverages, foods, candies, pharmaceutical products, perfumes, cosmetics, fragrances, aromatherapy, and as anti-microbial, antifungal, and antioxidant agents (ALI et al., 2015; KOSHIMA et al., 2015; KUMMER et al., 2013; LI et al., 2016; LOIZZO et al., 2016; MEHL et al., 2014; RUIZ-PÉREZ et al., 2016; RUSSO et al., 2015; SILVESTRE et al., 2016; SIMAS et al., 2017; TAO; JIA; ZHOU, 2014; TAO; OUYANG; JIA, 2014; XIAO et al., 2016).

The complexity of the essential oils composition can be observed in Table 3, where the chemical characterization of the volatile fraction of several citrus essential oils is shown. In this table we can observe that the citrus essential oils are mainly composed of terpene hydrocarbons, specially *d*-limonene, which corresponds to 37.07 – 96.05% of the whole essential oil volatile fraction, by weight. It is also possible to observe that the components most identified in the essential oils were the terpenes *d*-limonene,  $\alpha$ -pinene,  $\beta$ -pinene,  $\beta$ -myrcene,  $\beta$ -caryophyllene, the aldehydes neral and geranial, the alcohols linalool and  $\alpha$ -terpineol, and the ester neryl acetate, wick the chemical structures are presented in Figure 1.

Mandarin essential oils were predominantly composed of *d*-limonene (69.92 – 95.95%),  $\gamma$ -terpinene (20.04%, variety from Brazil),  $\beta$ -myrcene (1.68%), sabinene (0.99 – 1.80%), and  $\alpha$ -pinene (0.50 – 2.05%). The main compounds in bergamot essential oils were *d*-limonene (37.07 – 38.85%), linalyl acetate (21.41 – 34.71%), linalool (15.30 – 29.22%), and  $\gamma$ -terpinene (3.81 – 9.13%). The essential oils extracted from oranges peel were characterized as a mixture of essentially *d*-limonene (90.56 – 96.05%),  $\beta$ -myrcene (1.87 – 3.36%), and linalool (0.29 – 2.87%). Lemon essential oils were mainly composed of *d*-limonene (40.40 – 65.02%),  $\beta$ -pinene (2.90 – 23.36%),  $\gamma$ -terpinene (7.80 – 10.34%),  $\alpha$ -pinene (1.57 – 2.62%),  $\beta$ -bisabolene (0.73 – 3.18%), geranial (1.86 – 2.06%), neral (1.15 – 1.41%), and terpinen-4-ol (0.06 – 1.90%). Finally, the essential oil from acid limes were composed mainly of *d*-limonene (47.50 –

62.00%),  $\gamma$ -terpinene (11.80 – 17.00%),  $\beta$ -pinene (1.80 – 14.50%),  $\alpha$ -pinene (1.80 – 2.80%), geranial (0.60 – 6.40%),  $\alpha$ -terpineol (0.28 – 6.60%), and neral (0.56 – 4.70%).

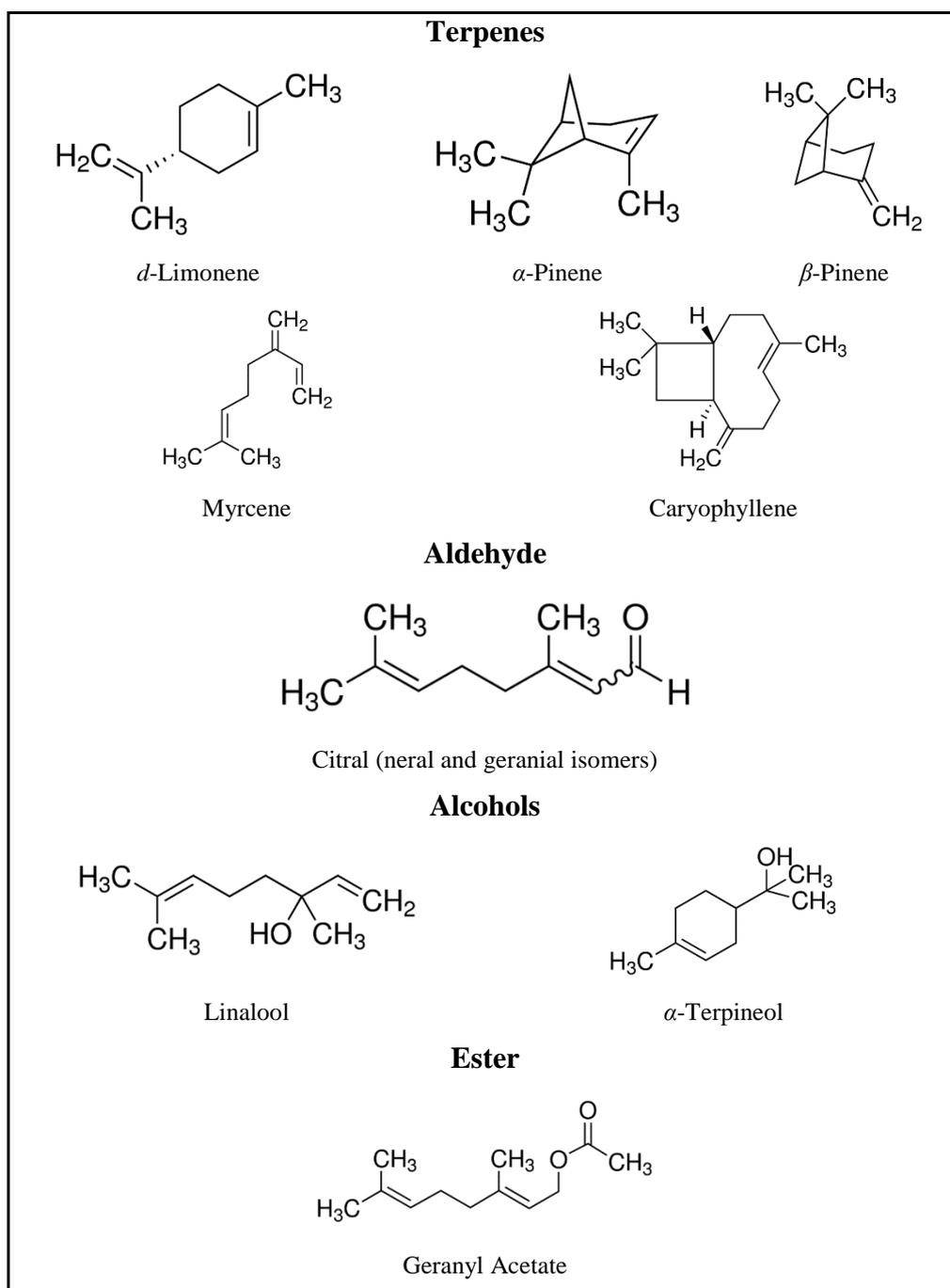


Fig. 1: Chemical structures of the main terpenes and oxygenated compounds found in citrus essential oils. From <http://www.sigmaaldrich.com>.

Differences in the essential oils compositions can be observed relating to their source and variety. The methods applied to extract and/or to identify the components may also have contributed for higher discrepancies. For instance, the essential oil of acid lime from Mexico

was reported as composed of 14.85% of  $\beta$ -thujene (RUIZ-PÉREZ et al., 2016), which was unidentified in other essential oils. The essential oil of acid lime from Cuba was composed of only 1.80% of  $\beta$ -pinene (PINO and ROSADO, 2001), which was abundant in other acid lime essential oils, and the acid lime essential oils from Brazil, described by Atti-Santos et al. (2005), had a high aldehydes content (11.10%). Curiously, these products were all obtained by hydro distillation. Orange, lemon and limes essential oils extracted by this technique were composed of lower terpene and higher alcohol and ether contents than the ones extracted by cold-pressing. On the other hand, orange essential oils extracted by hydro distillation were absent of aldehydes (ALLAF et al., 2013; RUIZ-PÉREZ et al., 2016).

**Table 3:** Chemical characterization of citrus essential oils volatile fraction.

	MM	Mandarin		Bergamot		Orange					Lemon				Acid Lime										
Scientific name	Cr	Cr	CaB	CbRP	CaB	Cad	Cs	Cs	Cs	Cs	nd	CaS	CaS	nd	nd	CIT	CIT	CIT	CIT	CIT	CIT				
Source	Sp <sup>a</sup>	Br <sup>a</sup>	It <sup>b</sup>	Br <sup>c</sup>	Br <sup>d</sup>	Br <sup>e</sup>	Fr <sup>f</sup>	Fr <sup>f</sup>	Me <sup>g</sup>	It <sup>h</sup>	It <sup>i</sup>	Cb <sup>j</sup>	Me <sup>k</sup>	It <sup>l</sup>	It <sup>h</sup>	Br <sup>c</sup>	Cb <sup>j</sup>	Br <sup>m</sup>	Br <sup>m</sup>	Me <sup>g</sup>	Br <sup>n</sup>	Me, Br, USA <sup>k</sup>			
Extraction procedure	CP	CP	CP	CP	CP	CP	HD	DIC	HD	CP	CP	HD	CP	CP	CP	CP	HD	HD	SC	HD	HD	CP			
<b>Terpenes</b>		<b>99.13</b>	<b>96.39</b>	<b>60.88</b>	<b>49.04</b>	<b>41.98</b>	<b>96.97</b>	<b>96.45</b>	<b>96.35</b>	<b>100.0</b>	<b>96.82</b>	<b>98.68</b>	<b>73.10</b>	<b>93.97</b>	<b>93.59</b>	<b>93.23</b>	<b>95.45</b>	<b>82.30</b>	<b>81.40</b>	<b>93.10</b>	<b>97.52</b>	<b>94.70</b>	<b>93.08</b>		
Nonane	128.3												0.01										<i>tr</i>		
$\alpha$ , $p$ -Dimethylstyrene	132.2											0.40					0.20								
2,4(10)-Thujadiene	134.2												0.01										<i>tr</i>		
Tricyclene	136.2												0.01										0.01		
$\alpha$ -Thujene	136.2				0.15					0.01	<i>tr</i>	<i>tr</i>	0.39	0.56	0.59	0.60	<i>tr</i>	0.50	0.80	0.48			0.56		
$\beta$ -Thujene	136.2																			14.85					
$\alpha$ -Pinene	136.2	0.50	2.05	1.60	0.64		0.51	0.95	0.66	0.80	0.98	0.53	2.10	2.45	1.57	2.62	2.13	1.80	1.90	2.70	2.17	2.80	2.10		
Camphene	136.2							0.02	<i>tr</i>			<i>tr</i>	1.30	0.12			0.70						0.06		
Sabinene	136.2	0.99	1.80	1.38	0.61		0.56				1.57	0.66			1.94		1.79		1.60	2.20					
$\beta$ -pinene	136.2			6.30	3.05							0.36		0.05	2.90	23.36	10.05	15.09	11.17	1.80	12.40	14.50	12.79	12.20	12.93
Carene	136.2						0.19																		
$\alpha$ -Myrcene	136.2																						1.43		
$\beta$ -Myrcene	136.2	1.69	1.68	1.48	0.94		2.30	2.44	2.53	2.80	3.36	1.87	2.10	1.26	1.85	1.94	1.51	2.60	1.20	1.40				1.44	
$\alpha$ -Phellandrene	136.2										0.04														
$\delta$ -3-Carene	136.2							0.12	0.12			0.14		0.01										0.01	
$\alpha$ -Terpinene	136.2										<i>tr</i>		0.26		0.27			0.30	0.40					0.27	
$\gamma$ -Terpinene	136.2		20.04	9.13	4.12	3.81				0.09	0.02	9.50	7.80	10.34	9.91	14.82	11.80	12.30	17.00	12.80	14.20	13.54			
$p$ -Cymene	136.2			0.23	0.41						<i>tr</i>	1.60	0.32				1.50	1.00			1.80	0.33			
$d$ -limonene	136.2	95.95	69.92	38.85	38.16	37.07	93.41	91.94	92.33	96.05	90.56	95.12	40.40	49.35	65.02	60.46	58.64	55.60	47.50	48.90	51.64	62.00	56.65		
( $Z$ )- $\beta$ -Ocimene	136.2													0.14		0.11								0.06	
( $E$ )- $\beta$ -Ocimene	136.2			0.37							0.04	0.04	0.50	0.39		0.18		<i>tr</i>						0.12	
Terpinolene	136.2			0.59						0.04	0.03		0.42	0.58	0.53		5.20							0.59	
$\alpha$ -Terpinolene	136.2		0.90		0.17							8.70					0.70		0.60	0.70					
$p$ -Mentha-3,8-diene	136.2											<i>tr</i>					<i>tr</i>								
$\alpha$ -Phellandrene	136.2												0.03											0.02	
Decane	142.3												<i>tr</i>											<i>tr</i>	
Dodecane	170.3													0.01										0.01	
Tridecane	184.4													0.02										<i>tr</i>	
$\beta$ -Elemene	204.4						0.02	0.02			0.02													0.07	
$\delta$ -Elemene	204.4												0.10	0.31										0.07	
( $E,E$ )- $\alpha$ -Farnesene	204.4											0.01	0.01											0.01	
( $E$ )- $\beta$ -Farnesene	204.4											0.01	0.10	0.13			<i>tr</i>			0.40				0.10	
$\alpha$ -Humulene	204.4						0.16	0.10				0.01	0.10												
Germacrene <i>B</i>	204.4													0.50										0.14	
Germacrene <i>D</i>	204.4						0.10	0.08				0.01	0.35											0.09	

	MM	Mandarin		Bergamot			Orange					Lemon				Acid Lime								
Scientific name		Cr	Cr	CaB	CbRP	CaB	Cad	Cs	Cs	Cs	Cs	nd	CaS	CaS	nd	nd	CIT							
Source		Sp <sup>a</sup>	Br <sup>a</sup>	It <sup>b</sup>	Br <sup>c</sup>	Br <sup>d</sup>	Br <sup>e</sup>	Fr <sup>f</sup>	Fr <sup>f</sup>	Me <sup>g</sup>	It <sup>h</sup>	It <sup>i</sup>	Cb <sup>j</sup>	Me <sup>k</sup>	It <sup>l</sup>	It <sup>h</sup>	Br <sup>c</sup>	Cb <sup>j</sup>	Br <sup>m</sup>	Br <sup>m</sup>	Me <sup>g</sup>	Br <sup>n</sup>	Me, Br, USA <sup>k</sup>	
<i>α</i> -Muurolene	204.4													0.12										0.05
<i>β</i> -Cubebene	204.4							0.07	0.06															
Valecene	204.4										0.11	0.04												
<i>α</i> -Cadiene	204.4										0.03													
<i>δ</i> -Cadinene	204.4							0.30	0.20		0.03	0.02												
<i>α</i> -Copanene	204.4							0.19	0.16		0.02	0.03												
<i>β</i> -Copanene	204.4										0.02													
<i>α</i> -Caryophyllene	204.4																		0.40					
<i>β</i> -Caryophyllene	204.4			0.54	0.45	0.41		0.14	0.09		0.02	0.01	0.70	1.07	0.44	0.31	0.65	0.10				1.70	0.58	
<i>α</i> -Bergamotene	204.4			0.41	0.31	0.28							0.90	0.09	0.48		1.26	<i>tr</i>	0.30	1.20	0.96			0.07
<i>β</i> -Bergamotene	204.4													1.36		0.49								1.11
<i>α</i> -Bisabolene	204.4													0.15					<i>tr</i>					0.12
<i>β</i> -Bisabolene	204.4				0.44								1.60	3.18	0.77	0.73	2.18	0.60	1.80	3.30				1.88
<i>β</i> -Chamigrene	204.4												0.10											
<i>β</i> -Santalene	204.4													0.05					<i>tr</i>					0.04
<i>β</i> -Chamigrene	204.4																		<i>tr</i>					
<i>α</i> -Selinene	204.4													0.11										0.04
<b>Aldehydes</b>		<b>0.13</b>	<b>0.60</b>		<b>0.45</b>	<b>0.31</b>	<b>0.73</b>				<b>1.42</b>	<b>0.88</b>		<b>3.51</b>	<b>3.47</b>	<b>3.59</b>	<b>3.35</b>		<b>11.10</b>	<b>1.80</b>	<b>0.56</b>	<b>2.20</b>	<b>3.89</b>	
Octanal	128.2						0.25				0.50	0.33				0.10								
Nonanal	142.2										0.10	0.05		0.02		0.13								0.01
Perillal	150.2							0.03				0.01												
Neral	152.2				0.18	0.11	0.04				0.10	0.05	1.15	1.41	1.20	1.26			4.70	0.70	0.56	1.60	1.34	
Geranial	152.2				0.27	0.20	0.09				0.15	0.08	1.86	2.06	1.95	2.09			6.40	1.10		0.60	2.27	
Citronellal	154.3						0.04				0.05	0.03	0.01		0.14									0.04
Decanal	156.3	0.13	0.30				0.28				0.38	0.23	0.21		0.05									0.08
Undecanal	170.3										0.02	0.01	0.03		0.02									0.01
Dodecanal	184.3										0.04	0.04	0.12											0.04
Tetradecanal	212.4												0.05											0.03
<i>β</i> -Sinensal	218.3		0.30								0.05	0.03												
<i>α</i> -Sinensal	218.3										0.03	0.02												
Hexadecanal	240.4													0.06										0.08
<b>Alcohols</b>		<b>0.41</b>	<b>0.14</b>	<b>16.66</b>	<b>15.30</b>	<b>29.46</b>	<b>1.35</b>	<b>3.25</b>	<b>3.54</b>		<b>0.77</b>	<b>0.35</b>	<b>24.00</b>	<b>1.45</b>	<b>0.72</b>	<b>0.46</b>	<b>0.17</b>	<b>14.30</b>	<b>5.70</b>	<b>1.10</b>		<b>2.30</b>	<b>0.99</b>	
Octanol	130.2											0.02	0.06											0.05
Nonanol	144.3													0.15										
Methylchavicol	148.2						0.56																	
<i>trans</i> -Pinocarveol	152.2													0.01										0.01
<i>trans</i> -Carveol	152.2						0.03						0.10						0.10					

	MM	Mandarin		Bergamot		Orange				Lemon				Acid Lime								
Scientific name	Cr	Cr	CaB	CbRP	CaB	Cad	Cs	Cs	Cs	Cs	nd	CaS	CaS	nd	nd	CIT						
Source	Sp <sup>a</sup>	Br <sup>a</sup>	It <sup>b</sup>	Br <sup>c</sup>	Br <sup>d</sup>	Br <sup>e</sup>	Fr <sup>f</sup>	Fr <sup>f</sup>	Me <sup>g</sup>	It <sup>h</sup>	It <sup>i</sup>	Cb <sup>j</sup>	Me <sup>k</sup>	It <sup>l</sup>	It <sup>h</sup>	Br <sup>c</sup>	Cb <sup>j</sup>	Br <sup>m</sup>	Br <sup>m</sup>	Me <sup>g</sup>	Br <sup>n</sup>	Me, Br, USA <sup>k</sup>
<i>cis</i> -Carveol	152.2											0.10					0.20					
<i>trans-p</i> -Mentha-2,8-dienol	152.2					0.06						0.01										<i>tr</i>
Linalool	154.3	0.41	0.14	16.66	15.30	29.22	0.60	2.62	2.87	0.68	0.29	0.30	0.17	0.26	0.14	0.17	0.10	1.30	0.20		0.90	0.18
Ocimenol	154.3					0.10																
$\alpha$ -Terpineol	154.3							0.18	0.28		0.07	0.04	12.70	0.28		0.22	6.60	2.20	0.40		1.40	0.28
<i>cis</i> - $\beta$ -Terpineol	154.3											2.20					2.20					
<i>trans</i> - $\beta$ -Terpineol	154.3																0.10					
$\gamma$ -Terpineol	154.3											1.60					0.40					
<i>cis</i> -Thujane-4-ol	154.3							0.37	0.30				0.04									
Terpinen-1-ol	154.3											2.30					1.90					
Terpinen-4-ol	154.3							0.08	0.09	0.01		1.90	0.52	0.31	0.06		1.30	1.20	0.50			0.08
Nerol	154.3				0.14								0.04					0.70				0.11
Geraniol	154.3									0.01			0.05		0.04			0.30				0.05
$\alpha$ -Fenchol	154.3											1.40					1.10					
$\beta$ -Fenchol	154.3												0.01									<i>tr</i>
Borneol	154.3											1.40	0.03				0.30					0.02
<i>cis</i> -2-Menthenol	154.3												0.02									0.01
2,3-Dimethyl-3-(4-methyl-3-pentenyl)-2-Norbornanol	222.4												0.07									0.05
Campherenol	222.4												0.07									0.06
$\alpha$ -Bisabolol	222.4												0.09									0.08
<b>Esters</b>		<b>0.43</b>	<b>22.39</b>	<b>35.21</b>	<b>28.06</b>		<b>0.03</b>	<b>0.05</b>			<b>0.01</b>	<b>0.10</b>	<b>0.37</b>	<b>0.46</b>	<b>1.31</b>	<b>1.05</b>	<b>0.60</b>	<b>0.30</b>	<b>0.40</b>	<b>0.99</b>		<b>1.33</b>
Methyl-N-methyl anthranilate	165.2	0.43																				
Octyl acetate	172.3										<i>tr</i>											
Linalyl acetate	196.3			21.41	34.71	27.09		0.03	0.05													
$\alpha$ -Terpinyl acetate	196.3			0.18																		
Neryl acetate	196.3			0.48	0.50	0.73				0.01	<i>tr</i>	0.08	0.46	0.61	1.05	0.50						1.00
Geranyl acetate	196.3			0.32		0.24						0.10	0.24		0.66	0.10	0.30	0.40				0.24
<i>cis</i> -Sabinene hydrate acetate	196.3																					0.04
<i>trans</i> -Sabinene hydrate acetate	196.3												0.04									0.05
Bornyl acetate	196.3												0.01									0.01
Citronellyl acetate	198.3									<i>tr</i>					0.04							
Geranyl propionate	210.3																					0.99

	MM	Mandarin		Bergamot		Orange				Lemon				Acid Lime									
Scientific name		Cr	Cr	CaB	CbRP	CaB	Cad	Cs	Cs	Cs	Cs	nd	CaS	CaS	nd	nd	CIT						
Source		Sp <sup>a</sup>	Br <sup>a</sup>	It <sup>b</sup>	Br <sup>c</sup>	Br <sup>d</sup>	Br <sup>e</sup>	Fr <sup>f</sup>	Fr <sup>f</sup>	Me <sup>g</sup>	It <sup>h</sup>	It <sup>i</sup>	Cb <sup>j</sup>	Me <sup>k</sup>	It <sup>l</sup>	It <sup>h</sup>	Br <sup>c</sup>	Cb <sup>j</sup>	Br <sup>m</sup>	Br <sup>m</sup>	Me <sup>g</sup>	Br <sup>n</sup>	Me, Br, USA <sup>k</sup>
<b>Ketones</b>								<b>0.08</b>	<b>0.04</b>			<i>tr</i>	<b>0.10</b>	<b>0.02</b>				<i>tr</i>			<b>0.93</b>	<b>0.02</b>	<i>tr</i>
Methylheptenone	126.2													<i>tr</i>								0.02	
Carvone	150.2											<i>tr</i>	0.10					<i>tr</i>					
<i>cis</i> -Pinocamphone	152.2													0.02									<i>tr</i>
Camphor	152.2							0.08	0.04														
Piperitone	152.2													<i>tr</i>									<i>tr</i>
4,8-Dimethylnona-3,7-Dien-2-one	166.3																				0.93		
Nootkatone	218.3											<i>tr</i>											
<b>Ether</b>							<b>0.19</b>	<b>0.15</b>				<b>0.01</b>	<b>2.50</b>	<i>tr</i>				<b>2.40</b>					<i>tr</i>
2,3-Dehydro-1,8-cineole	152.2													<i>tr</i>									<i>tr</i>
<i>cis</i> -Limonene oxide	152.2							0.09				<i>tr</i>											
<i>trans</i> -Limonene oxide	152.2							0.06				0.01											
Linaloyl oxide	154.2					0.19							0.50					0.60					
1,4-Cineolo	154.3												2.00					1.80					
<b>Others (unknown)</b>		<b>0.33</b>	<b>2.44</b>																				<b>1.20</b>

<sup>a</sup> Danielski et al. (2008); <sup>b</sup> Fantin et al. (2010); <sup>c</sup> Franceschi et al. (2004); <sup>d</sup> Koshima et al. (2015); <sup>e</sup> Martins et al. (2013); <sup>f</sup> Allaf et al. (2013); <sup>g</sup> Ruiz-Pérez et al. (2016); <sup>h</sup> Dugo et al. (1995); <sup>i</sup> Schipilliti et al. (2015); <sup>j</sup> Pino and Rosado (2001); <sup>k</sup> Dugo et al. (1997); <sup>l</sup> Benvenuti, Gironi and Lamberti (2001); <sup>m</sup> Atti-Santos et al. (2005); <sup>n</sup> Kummer et al. (2013); MM: molar mass (in g·mol<sup>-1</sup>); CP: Cold-pressing; HD: Hydrodistillation; DIC: Instant controlled pressure drop; SC: Supercritical extraction; nd: not defined; *tr*: traces; Cr: *Citrus reticulata*; CaBR: *Citrus aurantium Bergamia*; CbRP: *Citrus bergamia* Risso et Poit.; Cad: *Citrus aurantium dulcis*; Cs: *Citrus sinensis* (L.) Osbeck; CaS: *Citrus aurantifolia* Swingle; CIT: *Citrus latifolia* Tanaka; Sp: Spain; Br: Brazil; Fr: France; Me: Mexico; It: Italy; Cb: Cuba; USA: the United States of America.

### 2.3. Citrus essential oil fractionation process

As was already exposed in section 2.2, citrus essential oils are rich in terpene hydrocarbons and have huge differences in the oxygenated composition. According to reported by several authors, due to the presence of insaturations in the carbon chain (Fig. 1), the terpenes are more instable compounds, susceptible to oxidation and degradation reactions when exposed to light, heat or air, which may originate compounds with unpleasant aroma (off-flavors), denoting a product with low quality and low trade price. On the other hand, oxygenated compounds, such as alcohols and aldehydes are reported as more stable components and mainly responsible for citrus essential oil aroma (ARCE; SOTO, 2008; CHÁFER et al., 2005; DUGO et al., 1995; FISHER; SCOTT, 1997; KOSHIMA et al., 2012; PEREZ-CACHO; ROUSEFF, 2008; RAEISSI; PETERS, 2005a). Due to these facts, the fractionation process of citrus essential oil, aiming the separation between terpenes and oxygenated compounds, is interesting and necessary. A fractionated essential oil must present higher stability, better aroma qualities and higher solubility in water solutions (ARCE; SOTO, 2008; LAGO et al., 2014).

In the literature, it is possible to find several studies focused on the fractionation process of different citrus essential oils, which are presented in Table 4. Most techniques are supercritical fluid (CO<sub>2</sub>) and solvent extractions. The team led by Alberto Arce, in Spain, reported the use of different solvents, such as alcohols and ionic liquids, to provide the fractionation of essential oil mixtures, generally, a binary mixture of limonene and linalool. Among the solvents, the mixture of ethanol and water must be highlighted for numerous advantages: ethanol can be used in the preparation of beverages and perfumes (CHIYODA et al., 2011; GONÇALVES et al., 2014; KOSHIMA et al., 2012), improves the odor intensity and reduces oxidation reactions (CHÁFER et al., 2005; GIRONI; GONZALEZ FARIAS; LAMBERTI, 1995; LI; TAMURA, 2006), is a eco-friendly solvent (CAPELLINI et al., 2015), with low toxicity, low cost and abundance in Brazil (KOSHIMA et al., 2012, 2016). All these advantages have motivated our research group to study the fractionation of citrus essential oils using ethanol and water as solvents (CHIYODA et al., 2011; GONÇALVES, 2013; KOSHIMA et al., 2012, 2015). Part of the results are present in this document and discussed through the chapters.

**Table 4:** Studies focused on the fractionation process of citrus essential oils.

Citrus Essential Oil	Solvent	Fractionation Process	Assays	Results*	Reference
Orange and lemon peel oils		Supercritical (CO <sub>2</sub> ) desorption	Experimental	Comparison with the distillation process	(DUGO et al., 1995)
Limonene and citral	Ethanol and water mixtures	Solvent extraction	Experimental and modelling	LLE data	(GIRONI; GONZALEZ FARIAS; LAMBERTI, 1995)
Limonene + linalool mixtures		Supercritical (CO <sub>2</sub> ) desorption	Experimental and modelling	Optimum desorption conditions	(REVERCHON, 1997)
Lemon peel oil		Supercritical extraction (CO <sub>2</sub> )	Experimental and process simulation	VLE data	(BENVENUTI; GIRONI; LAMBERTI, 2001)
Limonene + linalool mixtures		Supercritical extraction (CO <sub>2</sub> )	Experimental and modelling	Solubility data	(CHÁFER et al., 2001)
Limonene + linalool mixtures	Diethylene glycol	Solvent extraction	Experimental and modelling	LLE data	(ARCE et al., 2002)
Limonene + linalool mixtures	1,2-propanediol and 1,3-propanediol	Solvent extraction	Experimental and modelling	LLE data	(ARCE; MARCHIARO; SOTO, 2003)
Limonene + citral, and limonene + linalool mixtures		Supercritical extraction (CO <sub>2</sub> )	Experimental	VLE data	(FONSECA; SIMOES; NUNES DA PONTE, 2003)
Limonene + linalool mixtures	2-aminoethanol	Solvent extraction	Experimental and modelling	LLE data	(ARCE; MARCHIARO; SOTO, 2004b)
Limonene, linalool, and limonene + linalool mixtures	Water	Solvent extraction	Experimental and modelling	LLE data	(ARCE; MARCHIARO; SOTO, 2004a)
<i>d</i> -Limonene	Ethanol and water mixtures	Solvent extraction	Experimental and modelling	LLE data	(CHÁFER et al., 2004)
Bergamot ( <i>Citrus aurantium</i> Bergamia Risso) peel oil		Supercritical extraction (CO <sub>2</sub> ) and vacuum distillation	Experimental	Purity, recovery, and color of oxygenated compounds	(FANG et al., 2004)
Acid lime ( <i>Citrus latifolia</i> Tanaka) and bergamot ( <i>Citrus bergamia</i> Risso et Poit.) peel oils		Supercritical extraction (CO <sub>2</sub> )	Experimental and modelling	VLE, LLE, and VLLE data	(FRANCESCHI et al., 2004)
Limonene + linalool mixtures	Water	Solvent extraction	Experimental and modelling	LLE data	(CHÁFER et al., 2005)
Limonene + linalool mixtures		Supercritical extraction (ethane)	Experimental	Phase transitions	(RAEISSI; PETERS, 2005a)
Limonene + linalool mixtures		Supercritical extraction (CO <sub>2</sub> )	Experimental	Phase transitions	(RAEISSI; PETERS, 2005b)
Limonene + linalool mixtures		Supercritical extraction (CO <sub>2</sub> )	Process simulation and optimization	Prediction of LLE, VLE and selectivity. Optimum process parameters	(DIAZ; ESPINOSA; BRIGNOLE, 2005)
Limonene + linalool mixtures	Ethanol and water mixtures	Solvent extraction	Experimental and modelling	LLE data	(ARCE et al., 2005)
Limonene + ethanol, linalool + ethanol, and limonene + linalool + ethanol mixtures		Supercritical extraction (CO <sub>2</sub> )	Experimental and modelling	VLE data	(IWAI et al., 2005)

Citrus Essential Oil	Solvent	Fractionation Process	Assays	Results*	Reference
Limonene + linalool mixtures	2-Butene-1,4-diol, ethylene glycol, and 1-ethyl-3-methylimidazolium methanesulfonate	Solvent extraction	Experimental and modelling	LLE data	(ARCE et al., 2006)
$\alpha$ -Pinene + $\beta$ -pinene + limonene mixtures	Ethanol and water mixtures	Solvent extraction	Experimental and modelling	LLE data	(LI; TAMURA, 2006)
Limonene + linalool mixtures	1-ethyl-3-methylimidazolium ethylsulfate ionic liquid	Solvent extraction	Experimental and modelling	LLE data	(ARCE et al., 2007)
Citral (neral + geranial)	Ethanol and water mixtures	Solvent extraction	Experimental	LLE data	(de DOZ et al., 2007)
Mandarin ( <i>Citrus reticulata</i> ) peel oils		Supercritical extraction (CO <sub>2</sub> )	Experimental	Folding ratios and optimal process conditions	(DANIELSKI et al., 2008)
Lemon peel oil		Supercritical extraction (CO <sub>2</sub> )	Modelling and process simulation	Prediction of process behavior	(GIRONI; MASCHIETTI, 2008)
$\alpha$ -Pinene + $\beta$ -pinene + limonene mixtures	1-Butanol and water or 1-propanol and water mixtures	Solvent extraction	Experimental and modelling	LLE data	(LI; TAMURA, 2008)
Limonene + linalool mixtures		Supercritical extractions (CO <sub>2</sub> and ethane)	Process simulation and optimization	Comparison between ethane and supercritical CO <sub>2</sub> . Optimal process conditions.	(RAEISSI et al., 2008)
Limonene + linalool mixtures	di-, tri-, or ethylene glycol, 1,2-propylene glycol	Solvent extraction	Experimental and modelling	LLE data	(SEVGILI; ŞAHIN; KIRBAŞLAR, 2008)
Limonene + linalool mixtures	Water	Solvent extraction	Experimental and modelling	LLE data	(de DOZ; CASES; SÓLIMO, 2008)
Limonene + octanal mixtures	1,3-Butanediol and 1,2-propenediol	Solvent extraction	Experimental and modelling	LLE data	(ROMERO et al., 2009)
Bergamot peel oil and limonene + linalool mixtures		Inclusion-based with solid deoxycholic acid (DCA)	Experimental	Physicochemical characterization	(FANTIN et al., 2010)
Limonene + linalool mixtures	1-ethyl-3-methylimidazolium 2-(2-methoxyethoxy) ethylsulfate ionic liquid	Solvent extraction	Experimental and modelling	LLE data	(FRANCISCO et al., 2010)
Limonene + linalool mixtures	1,3-butanediol	Solvent extraction	Experimental and modelling	LLE data	(ROMERO; DÍEZ; DÍAZ, 2010)
Limonene + linalool mixtures	1-Alkyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)amide ionic liquids	Solvent extraction	Experimental and modelling	LLE data	(LAGO et al., 2011)
Limonene + linalool + linalyl acetate mixtures	Ethanol and water mixtures	Solvent extraction	Experimental and modelling	LLE data	(CHIYODA et al., 2011)
Lemon peel oil	Ethanol and water mixtures	Solvent extraction and membranes	Experimental	Selection of best membrane conditions to provide higher interfacial stability	(DUPUY et al., 2011)
Orange peel oil	Ionic liquids	Solvent extraction	Experimental	Comparison with the distillation process	(BICA; GAERTNER; ROGERS, 2011)
Limonene + $\gamma$ -terpinene + $\beta$ -pinene + citral mixtures	Ethanol and water mixtures	Solvent extraction	Experimental and modelling	LLE data	(KOSHIMA et al., 2012)
Limonene + linalool mixtures	Alkylpyridinium alkylsulfate ionic liquids	Solvent extraction	Experimental and modelling	LLE data	(LAGO et al., 2012)
Orange peel oil		Short path evaporation	Experimental	Best operating conditions	(MARTINS et al., 2013)

Citrus Essential Oil	Solvent	Fractionation Process	Assays	Results*	Reference
Limonene + linalool mixtures	1-ethyl-3-methylimidazolium acetate and 1-butyl-3-methylimidazolium acetate ionic liquids	Solvent extraction	Experimental and modelling	LLE data	(LAGO et al., 2014)
Limonene + linalyl acetate + linalool; limonene + $\gamma$ -terpinene + $\beta$ -pinene + citral	Ethanol and water mixtures	Solvent extraction	Experimental and modelling	Physical properties (density and viscosity)	(FLORIDO et al., 2014)
Bergamot peel oil ( <i>Citrus aurantium bergamia</i> )	Ethanol and water mixtures	Solvent extraction	Experimental and modelling	LLE data	(KOSHIMA et al., 2015)
Mandarin ( <i>Citrus deliciosa</i> Tenore) peel oil		Vacuum fractional distillation	Experimental	Increasing on the concentration of specific components and thermal stability	(SILVESTRE et al., 2016)

\* LLE = liquid–liquid equilibrium, VLE = vapor–liquid equilibrium, VLLE = vapor–liquid–liquid equilibrium.

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### 3. OBJECTIVES

#### 3.1. General

The main objective of this work was to carry out the fractionation process of citrus essential oils by the solvent extraction technique, using ethanol/water mixtures as solvents. For that, this study was supported by four pillars: (i) obtainment of liquid–liquid equilibrium data of model and real systems, (ii) study of the physical properties of the phases from the liquid–liquid equilibrium; (iii) estimation of the aroma profile of crude essential oils and their phases from the liquid–liquid equilibrium; and (iv) fractionation of crude citrus essential oil (orange and acid lime) in a continuous equipment (perforated rotating disc contactor).

#### 3.2. Specifics

To accomplish the main objective, the following activities were developed:

- 1) Chemical characterization of crude citrus essential oils (orange and acid lime) in terms of the main volatile components;
- 2) Obtainment of liquid–liquid equilibrium data of model and real citrus essential oil systems:
  - a. Orange model systems composed of limonene + linalool + ethanol + water, at 298.2 K;
  - b. Lemon/lime model systems composed of  $\beta$ -pinene + limonene +  $\gamma$ -terpinene + citral + ethanol + water, at 298.2 K;
  - c. Orange real systems composed of crude orange essential oil + ethanol + water, at 298.2 K;
  - d. Acid lime real systems composed of crude acid lime essential oil + ethanol + water, at 298.2 K;
- 3) Adjustment of binary interaction parameters of the NRTL and UNIQUAC models for the orange model system data;
- 4) Prediction of the phases compositions from the liquid–liquid equilibrium of the orange real systems using the adjusted parameters of the NRTL and UNIQUAC models;
- 5) Prediction of the phases compositions from the liquid–liquid equilibrium of the acid lime real systems using the parameters of the NRTL model available in the literature;
- 6) Evaluation of the fractionation process of crude citrus essential oils (orange and acid lime) using ethanol/water mixtures as solvents in the PRDC equipment;

- 7) Determination of physical properties values of the phases from the liquid–liquid equilibrium, such as density, viscosity, and interfacial tension;
- 8) Correlation and calculation of the physical property values by thermodynamic or empirical models;
- 9) Obtainment of vapor–liquid equilibrium (headspace) of the phases from the liquid–liquid equilibrium of systems composed of crude citrus essential oils (orange and acid lime), ethanol, and water, at 298.2 K;
- 10) Characterization of the headspace of the crude citrus essential oils (orange and acid lime);
- 11) Experimental determination of the odor detection threshold (ODT) of citronellal, citral,  $\beta$ -pinene, and  $\gamma$ -terpinene by olfactometer;
- 12) Construction of the Perfumery Radars for the crude citrus essential oils (orange and acid lime) and for the phases from the liquid–liquid equilibrium.

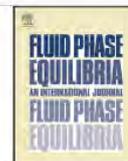
# CHAPTER I: Fractionation of orange essential oil using liquid–liquid extraction: Equilibrium data for model and real systems at 298.2 K.



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## Fractionation of orange essential oil using liquid–liquid extraction: Equilibrium data for model and real systems at 298.2 K.



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### ABSTRACT

Essential oils have many industrial applications and are basically composed of terpene hydrocarbons and oxygenated compounds. To improve their stability, sensorial quality, flavoring capacity and, consequently, their commercial value, the removal of hydrocarbon compounds is achieved by a fractionation process that can be performed by liquid–liquid extraction. In this work, a phase equilibrium study of real systems composed of crude orange essential oil and hydroalcoholic solvents (ethanol and water mixtures) was conducted and UNIQUAC and NRTL binary interaction parameters available in the literature were tested without success for the description of phase compositions. To obtain reliable parameters that provide a good description of the phase composition and can be used for computational simulation, liquid–liquid equilibrium data for model systems composed of limonene, linalool, ethanol and water at 298.2 K were determined and used to adjust new binary interaction parameters of UNIQUAC and NRTL thermodynamic models. Concerning the physical–chemical behavior of the system, the increase in the water content of solvent was observed to promote a decrease in the migration of oxygenated compounds to the solvent-rich phase and in the mutual solubility of the compounds. The increase in the composition of the oxygenated compounds in the system resulted in an increased solubility of these oxygenated compounds and a consequent decreased solvent selectivity. The new set of parameters provided a satisfactory representation of the experimental data, with global deviations of up to a 0.0031 mass fraction in the prediction process, which indicates that these parameters may be very useful in the optimization of the fractionation process by computational simulation.

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## I. Highlights

- Fractionation of crude orange essential oil using hydroalcoholic solvents.
- Liquid–liquid equilibrium data of model and real systems were determined.
- High deviations for phase compositions calculation using parameters from literature.
- New NRTL and UNIQUAC parameters were adjusted to model citrus systems.
- The distribution of essential oil compounds depends on solvent hydration level.

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## **I.1. Introduction**

Due to their therapeutic, antimicrobial and antioxidant activities, essential oils are widely used in the food and pharmaceutical industries. Essential oils are considered the primary raw materials of the fragrance and flavor industries [1-3].

Brazil is one of the major producers of essential oils, along with Madagascar, the United States of America, India, and China, which are also the main global producers [4]. The privileged position of Brazil is due to the production and exportation of citrus essential oils derived from such sources as oranges, of which Brazil is the main producer [4,5]. In 2012, orange fruits represented 63 % of the citrus production in the world; Brazil and the United States of America were responsible for 93 % of the global production of orange juice [6]. Currently, Brazil is the main exporter of frozen concentrated orange juice (FCOJ) in the world [4].

Citrus essential oils are characterized as mixtures of many components, including terpenes, sesquiterpenes, aldehydes, alcohols and esters, and can be described as a mixture of terpene hydrocarbons, oxygenated compounds and non-volatile residues [7, 8].

Terpenes are nonpolar compounds, with unsaturated hydrocarbons along the carbon chains of the molecules, which makes them susceptible to degradation reactions, such as polymerization (resulting in the formation of resins) and oxidation by exposure to air and light. This deterioration process can result in the so-called “off-flavor” industry term, causing significant changes to the original flavor of the essential oil [5, 9, 10]. The oxygenated compounds are generally preferable due to their characteristic flavors, indicating higher quality, and because of this preference, the content of oxygenated compounds has become an important parameter in determining the price of essential oils [11].

To improve the sensorial quality and stability of essential oils, some processes are applied to enrich the mixture with the oxygenated compounds. These processes are commonly known as “deterpenation”, which consists of the partial or total removal of terpene hydrocarbons (e.g., mainly limonene) from citrus essential oils [12, 13].

Crude orange essential oil (COEO), a mixture of more than 200 compounds, can be studied as a mixture of its two main components: limonene, as the terpene fraction, and linalool, as the oxygenated fraction. Linalool is difficult to separate from terpenes, because it is the key-component of the oxygenated fraction [14]. Several authors have published reports using mixtures composed of limonene and linalool to represent orange essential oils. In these studies,

different processes were employed to promote the separation between these compounds [11, 13, 15-25].

Among the diverse technologies applied to fractionation of essential oils, liquid–liquid extraction (or solvent extraction) has presented some advantages because the operation can be conducted without the use of heating (as in traditional distillation) or pressure changes (as in vacuum distillation or supercritical fluid extraction). Liquid–liquid extraction can therefore be a process that consumes a low level of energy [13] and does not significantly impact the sensory properties of the essential oils [19].

The liquid–liquid extraction separates some components present in a liquid solution by contact with another liquid; it is crucial that the two liquids that are directly contacted possess partial miscibility or immiscibility [26, 27]. In the context of the deterpenation or fractionation process, the use of ethanol as a solvent may be advantageous because ethanol shows high miscibility for linalool [9] and can be obtained at food grade quality. In addition, alcoholic extracts demonstrate high solubility in water, allowing their use in beverages and perfume formulations [28]. A few studies have reported that ethanol highlights the strength of the flavors of essential oils and reduces oxidation reactions [12, 28, 29].

In terms of phase equilibrium data and thermodynamic modeling, studies of the deterpenation of essential oils by liquid extraction have been conducted only on data from model systems, as only one report has been found concerning real systems (crude essential oils of bergamot and lavandin [30]).

The aim of this work was to report the liquid–liquid equilibrium (LLE) data for the real citrus systems composed of COEO, represented by terpenes and the oxygenated compounds, ethanol and water at 298.2 K. The thermodynamic parameters of the NRTL and UNIQUAC models for the citrus essential oil model systems (composed of limonene, linalool, ethanol and water) available in the literature [18] were used to calculate the composition of the phases from LLE. However, very unsatisfactory results were obtained from this prediction process.

Therefore, new citrus essential oil model systems, also comprising limonene, linalool, ethanol and water, as well as the model systems reported by Arce et al. [18], were prepared and were used to correlate new interaction parameters for the NRTL and UNIQUAC thermodynamic models. This new set of parameters was applied to calculate the phase compositions of the real systems, in terms of terpenes, oxygenated compounds, ethanol and water, and can be useful in studying the fractionation of orange essential oil by liquid–liquid

extraction using a computational simulation approach and in the design of equipment for this process.

## **I.2. Material and methods**

### **I.2.1. Materials**

Crude orange essential oil (COEO) was used to construct real systems while limonene and linalool (chromatography-grade products, supplied by Sigma-Aldrich, USA, with nominal purities exceeding 0.97 mass fraction) were used to construct citrus essential oil model systems. COEO was industrially extracted by cold pressing from the orange peels of a mixture of two varieties of *Citrus sinensis*, ‘Pera Rio’ and ‘Valencia’. The crude essential oil was processed and kindly donated by Louis Dreyfus Commodities (Bebedouro, SP, Brazil).

Hydroalcoholic solvents were prepared by diluting absolute ethanol with a nominal mass fraction purity exceeding 0.9950 (Merck, Darmstadt, Germany) with deionized water (Millipore, Milli-Q, Bedford, MA, USA). Solvents with water mass fractions of  $0.295 \pm 0.005$  and  $0.415 \pm 0.007$  were used to prepare the real systems with crude oil, and solvents with water mass fractions of  $0.235 \pm 0.002$ ,  $0.318 \pm 0.004$  and  $0.412 \pm 0.003$  were used to construct the model systems.

### **I.2.2. Apparatus and procedures**

#### **I.2.2.1. Characterization of chemical compounds**

Limonene, linalool and ethanol used in this work were chromatography-grade products. Their purities were verified by gas chromatography, and these chemicals were used without further purification. To check the purities and determine the retention times, limonene, linalool (Sigma-Aldrich, USA) and ethanol (Merck, Darmstadt, Germany) were analyzed by gas chromatography using a GC-FID (Shimadzu, model GC 2010 AF, Japan) with an automatic injector (Shimadzu, AOC 20i model, Japan). The analysis was performed using a nitroterephthalic acid-modified polyethylene glycol (DB-FFAP) capillary column ( $0.25 \mu\text{m}$ ,  $30 \text{ m} \times 0.25 \text{ mm}$  i.d.; Agilent, USA), helium gas carrier flow rate of  $1.13 \text{ mL}\cdot\text{min}^{-1}$ , an injection volume of  $1.0 \mu\text{L}$  with a split ratio of 1:50, an injection temperature of  $523.2 \text{ K}$ , an increasing column temperature of  $373.2$  to  $513.2 \text{ K}$  at a rate of  $8 \text{ K}\cdot\text{min}^{-1}$  and a detector temperature of  $553.2 \text{ K}$ .

The CAS numbers, purities and sources of the components used in the systems, COEO, limonene, linalool, ethanol and water are shown in Table 1. This table also shows the physical property values (density, dynamic viscosity and surface tension) related to these compounds, at  $298.2 \pm 0.1$  K.

The densities and viscosities were measured following the procedure previously adopted by Gonçalves et al. [31]. All density measurements were performed in triplicate, with the experimental uncertainties estimated to be less than or equal to 0.01. In the viscosity determinations, the uncertainty was estimated to be less than or equal to 0.03 mPa·s.

The surface tension was measured by a force tensiometer (Attension, model Sigma 702, Finland) with an accuracy of  $\pm 0.01$  mN·m<sup>-1</sup> and the temperature was controlled by an external thermostatic bath (accuracy of  $\pm 0.01$  K). A platinum Du Noüy ring was used for the determination of experimental surface tension. The value of the surface tension in the samples was automatically provided by the equipment when the ring broke the sample surface. All measurements were performed in quintuplicate, and the experimental uncertainties were up to 0.1 mN·m<sup>-1</sup>.

**Table 1:** Chemical names, CAS numbers, mass fraction purities, provenance of the materials and physical properties at the temperature  $T = 298.2$  K.<sup>a</sup>

Material	Chemical name	CAS registry number	Purity <sup>b</sup>	Molar mass / $\text{g}\cdot\text{mol}^{-1}$	Source	$\rho^c / \text{kg}\cdot\text{m}^{-3}$	$\eta^d / \text{mPa}\cdot\text{s}$	$\sigma^e / \text{mN}\cdot\text{m}^{-1}$	$r_i^f$	$q_i^g$
Limonene	1-methyl-4-prop-1-en-2-yl-cyclohexene	5989-27-5	0.9881	136.23	Sigma-Aldrich, USA	841.35	0.92	27.6	0.0461	0.0382
Linalool	(±)-3.7-Dimethyl-1.6-octadien-3-ol	78-70-6	0.9919	154.25	Sigma-Aldrich, USA	857.38	4.57	25.4	0.0487	0.0433
Ethanol	ethanol	64-17-5	0.9980	46.07	Merck, Germany	785.18	1.06	21.6	0.0559	0.0562
Water	water	7732-18-5	-	18.02	-	997.04	0.87	71.1	0.0511	0.0777
Crude Orange Essential Oil	-	-	-	-	Louis Dreyfus Commodities, Brazil	841.08	0.90	24.8	-	-

<sup>a</sup> Standard uncertainties  $u$  are  $u(T) = 0.1$  K,  $u(\rho) = 0.01$ ,  $u(\eta) \leq 0.03$  and  $u(\sigma) \leq 0.1$ .

<sup>b</sup> Experimentally determined by gas chromatography, given as mass fraction.

<sup>c</sup> Density.

<sup>d</sup> Viscosity.

<sup>e</sup> Surface tension.

<sup>f</sup> Volume structural parameter calculated according Eq. (6).

<sup>g</sup> Area structural parameter calculated according Eq. (6).

### I.2.2.2. Identification and quantification of crude orange essential oil compounds

Although essential oils contain hundreds of compounds, the composition of COEO was determined in terms of the components having mass fractions equal to or greater than 0.0001. The components present in COEO were identified using a gas chromatograph coupled to a mass spectrometer (GC-MS Shimadzu, model QP 2010 Plus, Japan) according to the similarity of mass spectra of COEO components to the reference mass spectra contained in the Solutions CG-MS software (version 2.5), based on the NIST 08 and NIST 08s libraries.

For accurate and reliable identification of the compounds, some hydrocarbons and oxygenates present in the COEO were also identified by comparison of the retention times of the pure compound injected under the same conditions as the sample.

Finally, the Kovats retention index was calculated for each compound identified according to Eq. (1), and the alkane standards C<sub>10</sub>-C<sub>40</sub> (Sigma-Aldrich, USA) were analyzed under the same conditions.

$$KI(x) = 100P_z + 100 \left[ \frac{\log RT(x) - \log RT(P_z)}{\log RT(P_{z+1}) - \log RT(P_z)} \right] \quad (1)$$

Where  $P_z$  is the number of carbons in the alkane immediately preceding the analyte,  $RT(x)$  is the analyte retention time,  $RT(P_z)$  is the retention time of the alkane immediately preceding the analyte, and  $RT(P_{z+1})$  is the retention time of the alkane immediately after the analyte. According to Adams [32], retention indices are useful for identifying a specific compound because the retention time may vary with different carrier gases and column age.

The conditions used in the CG-MS analysis were the same conditions that were used for the analysis by CG-FID, with the column interface temperature of 518.2 K, an ion source temperature of 473.2 K, a mass spectral scanning range from  $m/z$  40 to  $m/z$  800 and a 70 eV ion source energy.

After the identification of the compounds by GC-MS, the quantification of the constituents present in the COEO was performed by gas chromatography with a flame ionization detector (GC-FID, Shimadzu model GC 2010 AF, Japan) and an automatic injector (Shimadzu, model AOC 20i, Japan). The mass fractions of the compounds were calculated by internal normalization; compounds with mass fractions greater than 0.0001 were identified.

The chemical composition of COEO, in terms of compounds grouped as terpenes and oxygenated compounds, is presented in Table 2. In this table, the retention time and the Kovats index as well as the methodology used to identify each compound are also available.

### **I.2.2.3. Liquid–liquid Equilibrium (LLE)**

The phase equilibrium study was performed according to the procedure previously described by Gonçalves et al. [31]. For the real system preparation, different mass ratios (1/2, 1/1, 2/1, 3/1 and 4/1) of COEO to solvent (i.e., ethanol with  $0.295 \pm 0.005$  and  $0.415 \pm 0.007$  water mass fractions) were used to obtain different values of overall composition and, therefore, different tie lines. For the model systems, hydroalcoholic solvents with  $0.235 \pm 0.002$ ,  $0.318 \pm 0.004$  and  $0.412 \pm 0.003$  water mass fractions were used. The systems were prepared using a mass ratio of 1/1 (model citrus essential oil/ solvent), where the composition of the model citrus essential oil was prepared with different limonene and linalool mass proportions.

For the preparation of the systems, essential oil (COEO or limonene plus linalool mixtures) and solvent were weighed in a 15 or 50 mL polypropylene centrifuge tube (depending on the mass needed; Corning, USA), using an analytical balance with a readability and accuracy of 0.0001 g (Adam, model PW 254, Milton Keynes, UK). The tubes were sealed with parafilm (Pechinery Plastic Packaging, USA) and vigorously agitated at 2800 rpm for 10 minutes under room conditions (approximately 298 K and 0.1 MPa), to provide sufficient contact between the phases. To accelerate phase separation, the tubes were centrifuged at 5000 g for 30 minutes at  $298.2 \pm 1.5$  K in a centrifuge equipped with a temperature controller (Thermo Electron Corporation, model CR3i, France). Samples were then placed in a thermostatic bath (Marconi, model MA-184, Brazil) at  $298.2 \pm 0.1$  K for at least 20 hours. This contact time was selected on the basis of a previous study that showed the phase equilibrium was attained after 5 hours of rest. After this treatment, the two phases had clearly separated and had a well-defined interface.

Samples from both phases (the top terpene-rich phase and the bottom solvent-rich phase) were separately collected using syringes, and their compositions were determined. To quantify the contents of compounds of interest in the phases, the compounds were submitted for GC-FID analysis under the same conditions.

The identification of ethanol and terpenes and oxygenated compounds was conducted by comparing their retention times with the retention times of pure compounds; the quantification was performed by the external standard methodology. The water content in the phases was determined by Karl Fischer titration (Metrohm model 787 KF Titrino, Switzerland), using Karl Fischer reagents (CombiTitrant 5 mg·H<sub>2</sub>O·mL<sup>-1</sup>, Merck, Darmstadt, Germany). In this work, all measurements were performed at least in triplicate. Type A standard uncertainty [33] in the mass fractions was estimated to be less than or equal to  $0.5 \times 10^{-2}$ .

#### I.2.2.4. Experimental data validation test

The validity of the experimental data was evaluated by the procedure proposed by Marcilla et al. [34], in which  $i$  independent component balances can be written as shown in Eq. (2). In this equation,  $M_{OC}$  represents the amount of the overall composition (OC),  $M_{TP}$  and  $M_{SP}$  represent the masses of the terpene-rich (TP) and solvent-rich (SP) phases, respectively. The term  $w_{i,OC}$  represents the mass fraction of the component  $i$  in the OC,  $w_{i,TP}$  and  $w_{i,SP}$  represent the mass fraction of the component  $i$  in the TP and SP, respectively.

$$M_{OC} \cdot w_{i,OC} = M_{TP} \cdot w_{i,TP} + M_{SP} \cdot w_{i,SP} \quad (2)$$

With the application of a least-squares fitting procedure, the masses  $M_{TP}$  and  $M_{SP}$  were calculated using the experimental values  $w_{i,TP}$  and  $w_{i,SP}$ . The deviation ( $\delta$ ) between the calculated masses ( $M_{TP} + M_{SP}$ ) and  $M_{OC}$ , determined according to Eq. (3), along with OC, TP and SP composition, is shown in Tables 3 and 4 for the real and model systems, respectively.

$$\delta = \left( \frac{(M_{TP} + M_{SP}) - M_{OC}}{M_{OC}} \right) \times 100 \quad (3)$$

**Table 2:** Chemical composition of crude orange essential oil (COEO), Kovats Indices, molar masses and structural parameters  $r'_i$  and  $q'_i$ .

Component Group	Retention Time (min)	Identification <sup>a</sup>	K <sub>i</sub> <sup>b</sup>	Molar Mass / g mol <sup>-1</sup>	w <sub>i</sub> <sup>c</sup>	x <sub>i</sub> <sup>d</sup>	x <sub>j</sub> <sup>e</sup>	r <sub>i</sub> <sup>f</sup>	q <sub>i</sub> <sup>g</sup>
<b>Terpenes</b>				<b>136.26<sup>h</sup></b>	<b>0.9873</b>	<b>0.9882</b>	<b>1.0000</b>	<b>0.0461</b>	<b>0.0382</b>
<i>α</i> -Pinene	2.576	Standard	1487	136.23	0.0238	0.0238	0.0241	0.0444	0.0349
<i>d</i> -Limonene	2.848	Standard/ K <sub>i</sub>	1605	136.23	0.9628	0.9639	0.9754	0.0461	0.0382
Germacrene	6.003	NIST-MS (86 %) <sup>i</sup>	1871	204.35	0.0001	0.0000	0.0000	0.0472	0.0397
Cariophyllene	6.107	NIST-MS (89 %) <sup>i</sup> / K <sub>i</sub>	1876	204.36	0.0003	0.0002	0.0002	0.0450	0.0360
Valencene	7.445	NIST-MS (90 %) <sup>i</sup>	2036	204.35	0.0004	0.0003	0.0003	0.0450	0.0360
<b>Oxygenated Compounds</b>				<b>146.63<sup>h</sup></b>	<b>0.0127</b>	<b>0.0118</b>	<b>1.0000</b>	<b>0.0470</b>	<b>0.0408</b>
Octanal	3.225	Standard	1630	128.21	0.0028	0.0030	0.2506	0.0464	0.0393
Nonanal	3.953	NIST-MS (97 %) <sup>i</sup>	1671	142.24	0.0003	0.0003	0.0257	0.0465	0.0392
Citronellal	4.897	Standard	1819	154.25	0.0025	0.0022	0.1871	0.0458	0.0390
Linalool	5.247	Standard/ K <sub>i</sub>	1837	154.24	0.0044	0.0039	0.3332	0.0487	0.0433
Octanol	5.361	NIST-MS (97 %) <sup>i</sup>	1842	130.23	0.0007	0.0007	0.0591	0.0509	0.0448
Undecanal	6.057	NIST-MS (92 %) <sup>i</sup>	1873	170.29	0.0002	0.0001	0.0105	0.0468	0.0391
Neral	7.010	Standard/ K <sub>i</sub>	2015	152.23	0.0003	0.0003	0.0260	0.0449	0.0389
<i>α</i> -Terpineol	7.090	Standard K <sub>i</sub>	2019	154.25	0.0005	0.0004	0.0348	0.0414	0.0363
Dodecanal	7.241	NIST-MS (95 %) <sup>i</sup>	2026	184.32	0.0003	0.0002	0.0210	0.0469	0.0390
Geranial	7.603	Standard/ K <sub>i</sub>	2044	152.23	0.0007	0.0006	0.0521	0.0449	0.0389

<sup>a</sup> Identified by GC-MS.<sup>b</sup> Kovats Index, calculated according to Eq. (1).<sup>c</sup> Quantified by CG-FID internal normalization, in mass fraction.<sup>d</sup> Composition expressed in molar fraction.<sup>e</sup> Composition of the component *j* in the pseudocomponent *i* (terpenes or oxygenated compounds).<sup>f</sup> Volume structural parameter, calculated according to Eq. (4).<sup>g</sup> Area structural parameter, calculated according to Eq. (4).<sup>h</sup> Average molar mass of the pseudocomponent *i* (terpenes or oxygenated compounds).<sup>i</sup> Similarity between the sample spectrum and the component spectrum available at the NIST library, %.

**Table 3:** Experimental (liquid–liquid) equilibrium data for systems composed of crude orange essential oil (COEO), represented by terpenes (1) + oxygenated compounds (2) + ethanol (3) + water (4) for mass fractions  $w$  at the temperature  $T = 298.2$  K and pressure  $p = 0.1$  MPa.<sup>a</sup>

$w_{4S}^b$	OC <sup>c</sup>				TP <sup>d</sup>				SP <sup>e</sup>				$\delta^f / \%$
	$w_1$	$w_2$	$w_3$	$w_4$	$w_1$	$w_2$	$w_3$	$w_4$	$w_1$	$w_2$	$w_3$	$w_4$	
$0.295 \pm 0.005$	0.329	0.005	0.470	0.197	0.960	0.007	0.031	0.002	0.029	0.004	0.676	0.292	0.10
	0.328	0.005	0.470	0.197	0.960	0.007	0.031	0.002	0.032	0.003	0.671	0.294	0.23
	0.332	0.005	0.467	0.196	0.959	0.007	0.031	0.002	0.029	0.003	0.678	0.290	0.01
	0.327	0.005	0.471	0.197	0.960	0.006	0.032	0.002	0.033	0.004	0.679	0.284	0.19
	0.490	0.007	0.354	0.148	0.956	0.009	0.033	0.002	0.028	0.005	0.672	0.295	0.06
	0.493	0.007	0.352	0.148	0.956	0.009	0.033	0.002	0.030	0.005	0.673	0.291	0.04
	0.493	0.007	0.350	0.150	0.955	0.009	0.034	0.002	0.030	0.005	0.667	0.297	0.04
	0.656	0.010	0.236	0.099	0.953	0.011	0.034	0.002	0.026	0.006	0.664	0.304	0.01
	0.657	0.009	0.233	0.100	0.953	0.011	0.034	0.002	0.027	0.006	0.649	0.317	0.16
	0.738	0.011	0.176	0.075	0.953	0.012	0.033	0.002	0.024	0.007	0.652	0.317	0.02
	0.739	0.011	0.175	0.075	0.952	0.012	0.034	0.002	0.024	0.006	0.647	0.323	0.04
	0.789	0.011	0.140	0.060	0.953	0.013	0.032	0.002	0.026	0.007	0.635	0.332	0.04
	0.788	0.012	0.141	0.059	0.953	0.013	0.032	0.002	0.027	0.007	0.647	0.320	0.02
	0.788	0.011	0.140	0.060	0.952	0.013	0.034	0.002	0.024	0.006	0.636	0.334	0.02
$0.415 \pm 0.007$	0.330	0.005	0.382	0.283	0.965	0.010	0.023	0.002	0.008	0.002	0.563	0.427	0.02
	0.329	0.005	0.392	0.274	0.965	0.009	0.024	0.003	0.009	0.002	0.578	0.411	0.00
	0.493	0.007	0.288	0.211	0.961	0.012	0.025	0.002	0.007	0.003	0.558	0.432	0.08
	0.493	0.007	0.292	0.208	0.963	0.011	0.025	0.001	0.008	0.003	0.573	0.416	0.06
	0.655	0.009	0.195	0.141	0.960	0.012	0.025	0.003	0.008	0.003	0.553	0.436	0.02
	0.657	0.009	0.194	0.139	0.961	0.012	0.025	0.002	0.008	0.003	0.553	0.436	0.02
	0.739	0.011	0.145	0.106	0.957	0.013	0.026	0.003	0.007	0.003	0.538	0.453	0.02
	0.739	0.011	0.146	0.105	0.961	0.013	0.025	0.001	0.007	0.003	0.541	0.449	0.01
	0.739	0.011	0.146	0.105	0.961	0.013	0.025	0.001	0.008	0.003	0.544	0.445	0.01
	0.788	0.011	0.117	0.084	0.961	0.013	0.024	0.002	0.007	0.003	0.534	0.457	0.00
	0.788	0.011	0.118	0.082	0.961	0.013	0.024	0.001	0.006	0.003	0.539	0.452	0.01

<sup>a</sup> Standard uncertainties  $u$  are  $u(w) = 0.005$ ,  $u(T) = 0.1$  K, and  $u(p) = 10$  kPa.

<sup>b</sup> Water mass fraction in the solvent.

<sup>c</sup> Overall composition.

<sup>d</sup> Terpene-rich phase.

<sup>e</sup> Solvent-rich phase.

<sup>f</sup> Mass balance relative deviation, calculated according to Eq. (3), %.

**Table 4:** Experimental (liquid–liquid) equilibrium data for citrus essential oil model systems composed of [limonene (1) + linalool (2) + ethanol (3) + water (4)] for mass fractions  $w$  at the temperature  $T = 298.2$  K and pressure  $P = 0.1$  MPa.<sup>a</sup>

$w_{4S}^b$	OC <sup>c</sup>				TP <sup>d</sup>				SP <sup>e</sup>				$\delta^f / \%$
	$w_1$	$w_2$	$w_3$	$w_4$	$w_1$	$w_2$	$w_3$	$w_4$	$w_1$	$w_2$	$w_3$	$w_4$	
$0.235 \pm 0.002$	0.500	0.000	0.382	0.118	0.962	0.000	0.035	0.002	0.058	0.000	0.712	0.230	0.09
	0.499	0.000	0.383	0.118	0.962	0.000	0.036	0.002	0.057	0.000	0.713	0.230	0.08
	0.485	0.016	0.382	0.118	0.939	0.013	0.045	0.003	0.065	0.017	0.697	0.221	0.18
	0.485	0.016	0.382	0.118	0.937	0.013	0.047	0.003	0.066	0.017	0.689	0.228	0.12
	0.474	0.026	0.382	0.118	0.921	0.023	0.053	0.003	0.069	0.028	0.684	0.219	0.19
	0.475	0.026	0.382	0.118	0.921	0.022	0.054	0.003	0.070	0.027	0.681	0.223	0.04
	0.449	0.051	0.383	0.118	0.871	0.048	0.076	0.006	0.086	0.053	0.652	0.210	0.29
	0.450	0.051	0.382	0.117	0.870	0.048	0.077	0.006	0.084	0.051	0.649	0.216	0.11
	0.399	0.101	0.382	0.118	0.742	0.105	0.137	0.016	0.117	0.096	0.586	0.202	0.10
	0.401	0.100	0.382	0.118	0.748	0.104	0.133	0.015	0.114	0.094	0.593	0.198	0.32
	0.350	0.150	0.383	0.118	0.568	0.166	0.229	0.038	0.156	0.137	0.527	0.180	0.39
	0.349	0.150	0.383	0.118	0.568	0.164	0.228	0.039	0.151	0.134	0.527	0.188	0.19
$0.318 \pm 0.004$	0.500	0.000	0.341	0.159	0.973	0.000	0.025	0.002	0.030	0.000	0.655	0.315	0.00
	0.500	0.000	0.341	0.159	0.972	0.000	0.025	0.003	0.015	0.000	0.661	0.323	0.13
	0.484	0.016	0.341	0.159	0.945	0.016	0.036	0.003	0.028	0.015	0.639	0.319	0.16
	0.477	0.015	0.347	0.161	0.946	0.015	0.035	0.004	0.033	0.014	0.643	0.310	0.08
	0.474	0.025	0.342	0.159	0.928	0.026	0.042	0.004	0.035	0.022	0.636	0.308	0.22
	0.475	0.025	0.341	0.159	0.928	0.026	0.043	0.003	0.033	0.021	0.625	0.321	0.11
	0.475	0.025	0.350	0.150	0.921	0.026	0.049	0.003	0.036	0.021	0.642	0.301	0.06
	0.451	0.050	0.340	0.159	0.870	0.057	0.067	0.006	0.029	0.040	0.610	0.322	0.22
	0.450	0.051	0.341	0.159	0.872	0.057	0.065	0.006	0.041	0.040	0.607	0.312	0.07
	0.447	0.050	0.351	0.151	0.863	0.057	0.074	0.006	0.038	0.040	0.631	0.291	0.31
	0.400	0.100	0.341	0.159	0.744	0.123	0.117	0.016	0.050	0.071	0.567	0.312	0.03
	0.400	0.101	0.341	0.159	0.742	0.125	0.118	0.016	0.051	0.069	0.565	0.314	0.00
0.349	0.150	0.342	0.159	0.582	0.191	0.191	0.036	0.052	0.092	0.538	0.317	0.12	
0.349	0.150	0.342	0.159	0.576	0.194	0.191	0.038	0.051	0.090	0.537	0.321	0.04	

$w_{4S}^b$	OC <sup>c</sup>				TP <sup>d</sup>				SP <sup>e</sup>				$\delta^f / \%$
	w <sub>1</sub>	w <sub>2</sub>	w <sub>3</sub>	w <sub>4</sub>	w <sub>1</sub>	w <sub>2</sub>	w <sub>3</sub>	w <sub>4</sub>	w <sub>1</sub>	w <sub>2</sub>	w <sub>3</sub>	w <sub>4</sub>	
0.412 ± 0.003	0.500	0.000	0.286	0.214	0.979	0.000	0.019	0.002	0.008	0.000	0.549	0.444	0.13
	0.500	0.000	0.290	0.209	0.979	0.000	0.020	0.001	0.010	0.000	0.569	0.421	0.02
	0.485	0.015	0.286	0.214	0.948	0.020	0.029	0.003	0.011	0.009	0.552	0.428	0.09
	0.485	0.015	0.286	0.214	0.947	0.020	0.030	0.003	0.010	0.009	0.563	0.418	0.27
	0.485	0.016	0.294	0.205	0.944	0.021	0.033	0.002	0.010	0.009	0.577	0.404	0.28
	0.474	0.026	0.286	0.214	0.925	0.034	0.037	0.003	0.011	0.014	0.547	0.428	0.22
	0.472	0.025	0.287	0.215	0.925	0.035	0.036	0.004	0.011	0.014	0.540	0.435	0.04
	0.470	0.025	0.298	0.208	0.922	0.034	0.041	0.002	0.010	0.013	0.568	0.409	0.24
	0.450	0.050	0.286	0.214	0.866	0.072	0.056	0.006	0.012	0.024	0.535	0.429	0.24
	0.450	0.050	0.295	0.205	0.859	0.072	0.063	0.006	0.010	0.023	0.557	0.410	0.31
	0.400	0.101	0.286	0.214	0.726	0.151	0.107	0.016	0.012	0.038	0.515	0.435	0.30
	0.399	0.100	0.286	0.215	0.726	0.152	0.107	0.015	0.011	0.037	0.508	0.444	0.16
	0.398	0.100	0.295	0.207	0.727	0.149	0.111	0.014	0.012	0.035	0.518	0.435	0.30
	0.375	0.125	0.285	0.214	0.654	0.191	0.133	0.021	0.011	0.041	0.497	0.451	0.12
	0.375	0.125	0.286	0.214	0.649	0.192	0.137	0.022	0.011	0.042	0.503	0.445	0.18
	0.375	0.125	0.294	0.206	0.655	0.188	0.136	0.020	0.010	0.037	0.512	0.441	0.29
	0.350	0.150	0.286	0.214	0.577	0.226	0.163	0.034	0.009	0.039	0.462	0.490	0.09
	0.353	0.149	0.285	0.213	0.585	0.226	0.160	0.030	0.008	0.040	0.484	0.468	0.12
	0.350	0.150	0.294	0.206	0.581	0.222	0.170	0.027	0.007	0.035	0.479	0.478	0.13

<sup>a</sup> Standard uncertainties  $u$  are  $u(w) = 0.005$ ,  $u(T) = 0.1$  K, and  $u(p) = 10$  kPa.

<sup>b</sup> Water mass fraction in the solvent.

<sup>c</sup> Overall composition.

<sup>d</sup> Terpene-rich phase.

<sup>e</sup> Solvent-rich phase.

<sup>f</sup> Mass balance relative deviation, calculated according to Eq. (3), %.

### I.2.3. Thermodynamic modeling procedure

#### I.2.3.1. Phase composition calculation using parameters from the literature

As previously mentioned, the thermodynamic parameters of NRTL [35] and UNIQUAC [36] models for the citrus essential oil model systems (composed of limonene, linalool, ethanol and water) available in the literature [18] were used to calculate the phase compositions of the real systems, composed of COEO and hydroalcoholic solvents, at 298.2 K, experimentally determined in this work.

COEO was considered as a mixture of two groups of components, terpenes and oxygenated compounds; crude oil was treated in this work as a mixture of two pseudo-compounds with the average molar masses indicated in Table 2. Therefore, the volume and area parameters ( $r'_i$  and  $q'_i$ ) for the pseudo-components were calculated according to Eq. (4) and are also shown in Table 2. In this equation,  $v_k^{(j)}$  is the number of groups  $k$  in the molecule of the component  $j$  in the pseudo-component  $i$ ;  $M_i$  is the average molar mass of the pseudo-component  $i$ ;  $G$  is the total number of groups;  $C$  is the number of components  $j$  in the pseudo-component  $i$ ;  $x_j$  is the molar fraction of the component  $j$  in the pseudo-component  $i$ ; and the terms  $R_k$  and  $Q_k$  are the van der Waals parameters [37].

$$r'_i = \frac{1}{M_i} \sum_j^C x_j \sum_k^G v_k^{(j)} R_k \quad q'_i = \frac{1}{M_i} \sum_j^C x_j \sum_k^G v_k^{(j)} Q_k \quad (4)$$

The procedure for the calculation of the phase composition involves flash calculations for the overall composition (OC) of the experimental tie lines, according to the procedure developed by Stragevitch and d'Avila [38].

The deviation between the experimental and the calculated compositions in the terpene-rich (TP) and solvent-rich (SP) phases was calculated by Eq. (5).

$$\Delta w = \sqrt{\frac{\sum_{n=1}^N \sum_{i=1}^K \left[ \left( w_{i,n}^{TP,exptl} - w_{i,n}^{TP,calcd} \right)^2 + \left( w_{i,n}^{SP,exptl} - w_{i,n}^{SP,calcd} \right)^2 \right]}{2NK}} \quad (5)$$

where  $N$  represents the total number of tie lines,  $K$  represents the total number of components,  $w$  represents the mass fraction, the subscripts  $i$  and  $n$  represent the component and tie line, respectively, and the superscripts TP and SP represent the terpene and solvent phases, respectively. The superscripts exptl and calcd refer to the experimental and calculated compositions.

### I.2.3.2. Adjustment procedure for new binary interaction parameters

The experimental phase-equilibrium model data obtained using limonene and linalool mixtures and hydroalcoholic solvents with water mass fractions of  $0.235 \pm 0.002$ ,  $0.318 \pm 0.004$  and  $0.412 \pm 0.003$  were used to adjust the new binary interaction parameters of the NRTL and UNIQUAC equations. These systems were treated as quaternary systems composed of limonene (1) + linalool (2) + ethanol (3) + water (4).

In the parameters adjustment procedure, mass fractions were adopted as the composition unit, as previously suggested by Oliveira et al. [39]. For further information, Oliveira et al. [39] show the isoactivity criterion of LLE, developed on a molar fraction basis, expressed on a mass fraction basis, and Chiyoda et al. [40] and Oliveira et al. [41] show the activity coefficient equations, expressed in mass fractions, according to the NRTL and UNIQUAC models, respectively.

The volume and area parameters ( $r_i$  and  $q_i$ ) for these pure compounds (limonene, linalool, ethanol and water) are shown in Table 1. These parameters, necessary for the UNIQUAC model, were converted to a mass fraction basis, using Eq. (6). In this equation,  $v_k^i$  is the number of groups  $k$  in the molecule of the component  $i$ ,  $M_i$  is the molar mass of the compound  $i$ ,  $G$  is the total number of groups, and the terms  $R_k$  and  $Q_k$  are the van der Waals parameters obtained from Magnussen et al. [37].

$$r_i = (1/M_i) \sum_k^G v_k^i R_k \quad q_i = (1/M_i) \sum_k^G v_k^i Q_k \quad (6)$$

The estimation of UNIQUAC and NRTL parameters ( $A_{ij}$ ,  $A_{ji}$ ,  $B_{ij}$ ,  $B_{ji}$ , and  $\alpha_{ij}$  respectively) was performed according to the procedure reported by Stragevitch and d'Avila [38].

$$OF(w) = \sum_{m=1}^D \sum_{n=1}^N \sum_{i=1}^{K-1} \left\{ \left[ \left( w_{i,n,m}^{TP,exptl} - w_{i,n,m}^{TP,calcd} \right) / \sigma_{w_{i,n,m}^{TP}} \right]^2 + \left[ \left( w_{i,n,m}^{SP,exptl} - w_{i,n,m}^{SP,calcd} \right) / \sigma_{w_{i,n,m}^{SP}} \right]^2 \right\} \quad (7)$$

where  $D$ ,  $N$  and  $K$  are the total numbers of data groups, tie lines and components, respectively, in the group of data  $m$ . The term  $w$  is the mass fraction, where the subscripts  $i$ ,  $n$  and  $m$  represent the component, tie line and group number, respectively. The superscripts *exptl* and *calcd* refer to the experimental and calculated compositions, respectively. The terms  $\sigma_{w_{i,n,m}^{TP}}$  and  $\sigma_{w_{i,n,m}^{SP}}$  are the standard deviations of the two liquid phase compositions.

The deviation between the experimental and calculated compositions in both phases was also calculated according to Eq. (5).

### **I.2.3.3. Phase composition calculation using new interaction binary parameters**

The composition of the phases of the real systems (composed of COEO and hydroalcoholic solvent) was calculated using the new sets of parameters that were adjusted to the model systems according to item 2.3.2. The procedure for the calculation of the phase composition was the same as the procedure previously shown in the item 2.3.1, where parameters from Arce et al. [18] were used.

## **I.3. Results and Discussion**

### **I.3.1. Characterization of pure compounds and chemical composition of crude orange essential oil (COEO)**

Table 1 shows the chemical names, CAS numbers, the molar masses, source, physical property values (density, viscosity and surface tension) and experimental purity for each compound considered in the experiments.

The values of the purity of limonene, linalool and ethanol, experimentally determined by gas chromatography, are in agreement with values declared by the suppliers in the product specification reports ( $\geq 0.97$  for limonene and linalool and  $\geq 0.995$  for ethanol). Physical property values (at 298.2 K), shown in Table 1, are in agreement with those reported in the literature, for the density and viscosity values of limonene [18,42], linalool [18,42] ethanol and water [18] and the surface tension of the pure components [43]. Physical properties of COEO at 298.2 K, also available in Table 1, were not found in the literature.

The COEO composition evaluated by GC-MS is shown in Table 2, in which 15 main compounds were identified. As reported in the literature [5], the COEO was composed mainly of limonene, having a mass fraction of more than 0.90 of the essential oil. In Table 1, COEO shows values for density and viscosity very close to those of limonene, showing that this terpene is the major component of the crude orange essential oil.

As previously mentioned, the identification method was based on the comparison of the mass spectrum obtained with the data available in the NIST 08 and NIST 08s libraries and on the comparison with retention times of standards injected under the same analytical conditions. Some Kovats index (KI) values corresponding to the conditions employed in the chromatographic analysis were found in the literature [30] and were used to identify some

compounds present in the COEO sample (Table 2). Other KI values for the DB-FFAP column calculated by Eq. (1), not reported in the literature and provided in Table 2, can be used by other authors to identify the compounds present in samples when columns with polar phases are used.

Table 2 shows that the compounds in COEO can be clustered into two fractions, the terpene fraction in which limonene is the major compound and the oxygenated compound fraction with linalool as the major representative component. This approach allows us to propose a description of COEO as a pseudo-compound in which these two fractions are treated as two pseudo-components with terpene and oxygenated fractions having average molar masses.

This approach assumes that the different terpenes present in the terpene fraction behave in a way that is very similar to the liquid–liquid system under analysis. In this case, such components can be adequately replaced by a pseudo-compound having the corresponding average physical chemical properties. This approach was previously adopted with success by Koshima et al. [44] in the fractionation study of lemon oil model systems.

The same hypothesis is employed for the mixture of oxygenated compounds. Such a hypothesis will be tested by the adjustment of parameters to the model systems and the subsequent use of these parameters in the equilibrium prediction for systems containing crude orange essential oil.

In this way, real systems composed of COEO and hydroalcoholic solvents were treated as terpene compounds (1) + oxygenated compounds (2) + ethanol (3) + water (4) in pseudo-quaternary systems.

### **I.3.2. Liquid–liquid equilibrium data for real systems and phase composition calculation using NRTL and UNIQUAC parameters available in the literature**

As previously reported, the overall phase compositions and the corresponding tie lines for the real systems composed of terpenes (1), oxygenated compounds (2), ethanol (3) and water (4) at  $298.2 \pm 0.1$  K are shown in Table 3, where all compositions are given as mass fractions.

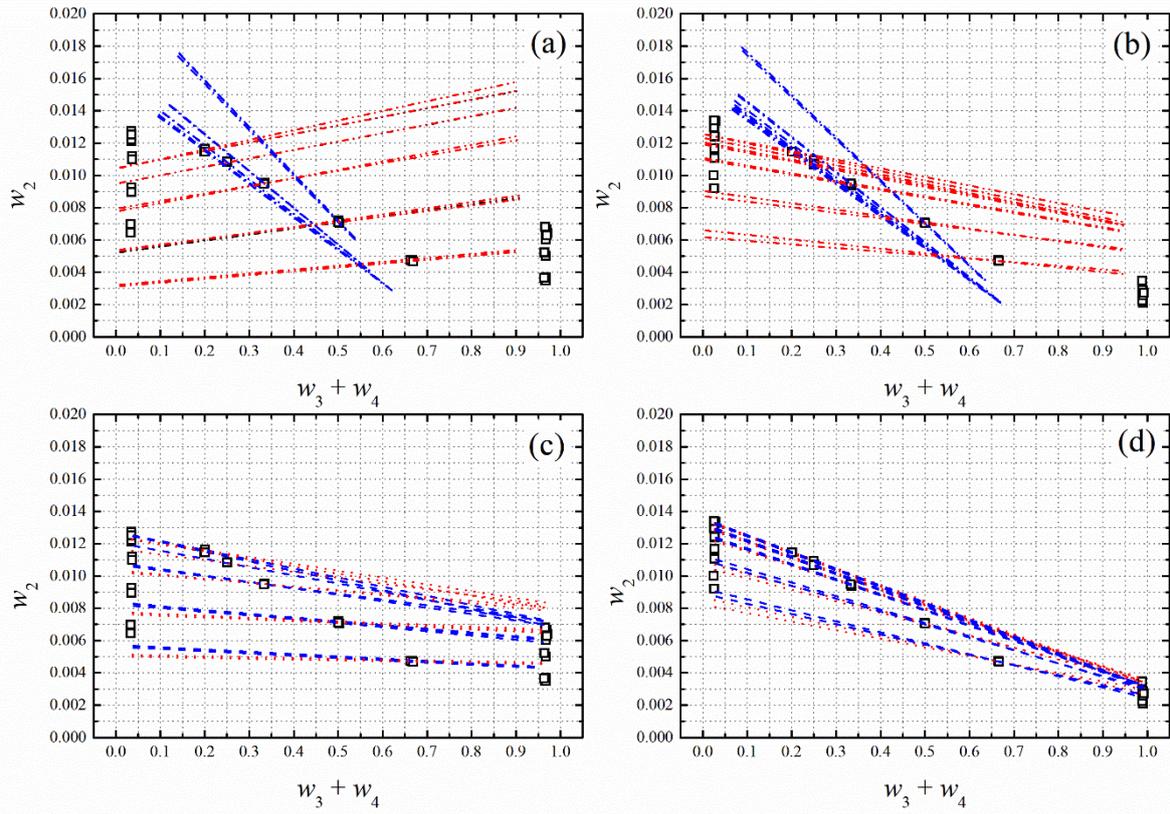
Figure 1 shows equilibrium diagrams for two different levels of water in the solvent [ $0.295 \pm 0.005$  (Figure 1a) and  $0.415 \pm 0.007$  (Figure 1b)]. In these equilibrium diagrams, ethanol and water were assumed to be a single solvent, only for qualitative purposes, allowing the representation of the pseudo-quaternary systems in rectangular coordinates. In these diagrams, the mass fraction composition of the terpene fraction can be obtained by difference.

In the experimental data, the increase of water content in the solvent leads to a lower migration of the oxygenated compounds present in the COEO to the solvent phase. The increase

in the level of water in the solvent causes a slight expansion of the phase splitting region. This expansion is due mainly to the minimization of solubility of the terpenic hydrocarbon fraction in the solvent-rich phase.

The utility of the binary interaction parameters of the NRTL and UNIQUAC models, available in the literature [18], was tested in the description of the distributions of the compounds between the liquid phases. These calculated data are also shown in Figure 1. The set of parameters in the NRTL model failed primarily in the description of the solubility of the phases, especially in the prediction of the terpene fraction solubility in the solvent-rich phases. This set of parameters also failed in the description of oxygenated compound distribution, underestimating the extraction of this fraction. However, the UNIQUAC parameter set suggested by Arce et al. [18] overestimated the oxygenated compounds extraction.

The mean standard deviation, calculated by Eq. (5), related to the prediction process using the binary interaction parameters proposed by Arce et al. [18] is shown in Table 5. According to the values previously observed in Figure 1, supported by the high deviation values shown in Table 5, the phase composition calculation related to systems composed of crude orange oil can be inferred not to be satisfactory, requiring additional efforts related to the adjustment of new interaction parameters.



**Fig. 1** - Equilibrium diagrams for the real systems composed of crude orange essential oil (COEO), represented by terpenes (1), oxygenated compounds (2), ethanol (3) and water (4), at  $(298.2 \pm 0.1)$  K. (a and b) Calculated by prediction procedure using parameters from [18]:  $-\cdot-\cdot-$ , NRTL model;  $\cdot-\cdot-\cdot$ , UNIQUAC model; (c and d) Calculated by prediction procedure using the new parameters from Table 6:  $-\cdot-\cdot-$ , NRTL model;  $\cdot-\cdot-\cdot$ , UNIQUAC model. (a and c)  $w_{4S} = 0.295 \pm 0.005$ ; (b and d)  $w_{4S} = 0.415 \pm 0.007$ .

**Table 5:** Mean deviations between experimental and calculated compositions in the phases.

$w_{4S}^a$	$\Delta w^b$			
Correlation procedure	NRTL		UNIQUAC	
$0.235 \pm 0.002$	0.0066		0.0122	
$0.318 \pm 0.004$	0.0120		0.0075	
$0.412 \pm 0.003$	0.0043		0.0051	
Global Deviation	0.0081		0.0082	
Prediction procedure	NRTL		UNIQUAC	
	Arce et al. [18]	New parameters	Arce et al. [18]	New parameters
$0.295 \pm 0.005$	0.2235	0.0035	0.0288	0.0033
$0.415 \pm 0.007$	0.1910	0.0025	0.0641	0.0016
Global Deviation	0.2098	0.0031	0.0476	0.0027

<sup>a</sup> Water mass fraction in the solvent.<sup>b</sup> Calculated according to Eq. (5).**Table 6:** New UNIQUAC and NRTL parameters estimated in this work, at the temperature  $T = (298.2 \pm 0.1)$  K.

Pair $ij^a$	UNIQUAC model		NRTL model		
	$A_{ij}^b/K$	$A_{ji}/K$	$B_{ij}^c/K$	$B_{ji}/K$	$\alpha_{ij}$
12	-25.277	0.25023	49.473	-714.27	0.18
13	353.92	-88.182	218.98	470.81	0.10
14	777.37	502.60	448.37	5907.2	0.11
23	-129.94	139.24	-1315.6	1226.2	0.21
24	-190.11	909.72	-523.64	2078.0	0.39
34	205.07	-145.05	-10.641	64.505	0.10

<sup>a</sup> Limonene (1), linalool (2), ethanol (3) and water (4).<sup>b</sup>  $\Delta u_{ij}/R$ .<sup>c</sup>  $\Delta g_{ij}/R$ .

### I.3.3. Liquid–liquid equilibrium data for model citrus systems and new binary interaction parameters for NRTL and UNIQUAC equations

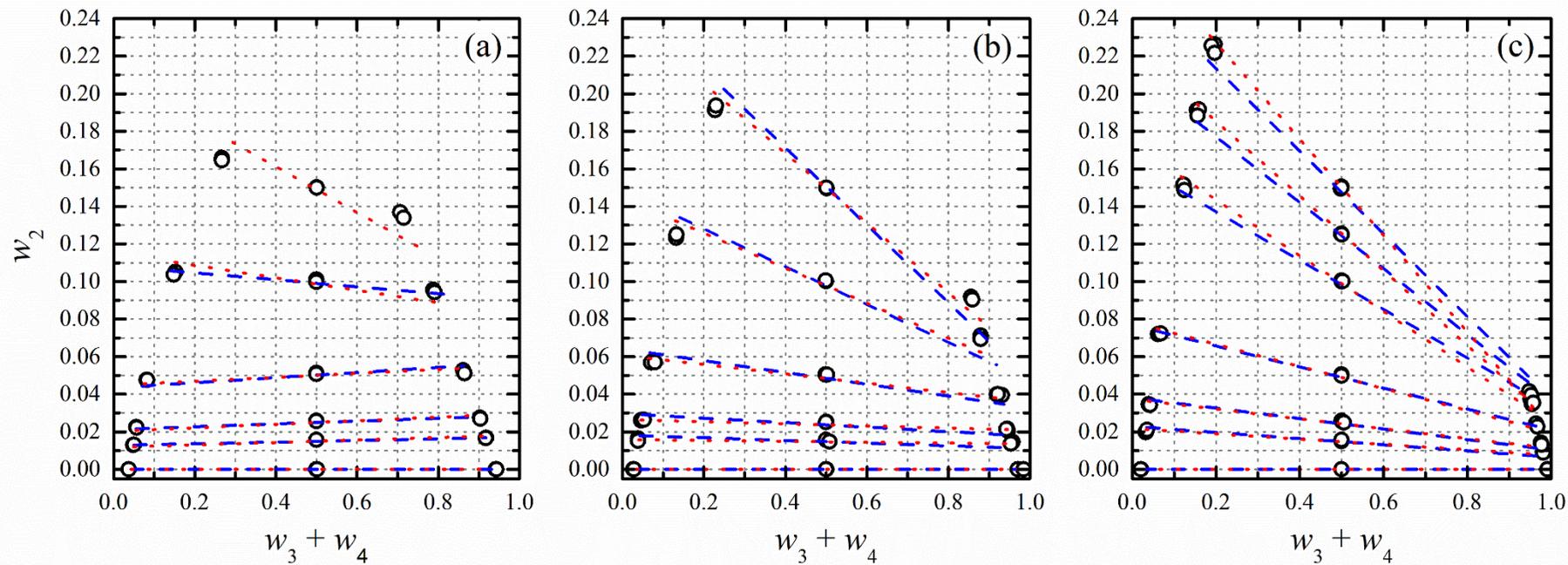
As previously discussed in item 2.3.2, model systems composed of limonene (1), linalool (2), ethanol (3) and water (4) were experimentally determined and used to adjust new binary interaction parameters for NRTL and UNIQUAC models. In Figure 2, these LLE experimental data are presented in equilibrium diagrams for the three solvents studied (ethanol with  $0.235 \pm 0.002$  of a water mass fraction, Figure 2a;  $0.318 \pm 0.004$ , Figure 2b; and  $0.412 \pm 0.003$ , Figure 2c).

In Figure 2, as well as in Figure 1, a good alignment is observed between the experimental data sets, relative to both overall and phase composition. Tie lines based on the experimental data were determined by the linear regression of each corresponding set of overall, terpene-

rich, and solvent-rich phase compositions. Correlation coefficients higher than 99.5 % were obtained for all tie lines, indicating a low error in the experimental determination of the tie line compositions. The good quality of the measured experimental data was confirmed by the small deviations in the mass balances (from 0.0 up to 0.39 %) as well as the low experimental data uncertainty ( $u(w) \leq 0.005$ ).

In these phase diagrams, the increase of water in the solvent causes a decrease in the extraction of the components of the system, as previously observed for real systems (Figure 1). An increase of the water content in the solvent leads to a decreased ability of the solvent to extract the essential oil compounds, as previously reported in the literature [31, 39, 40, 44]. This observation was valid for model systems composed of limonene and linalool and for real systems composed of crude essential oil. Doz et al. [22] reported that the solubility values of binary mixtures of limonene-water and linalool-water were very small. This observation led us to infer that water decreases the solubility among the compounds present in the system (i.e., limonene, linalool and ethanol). Relative to the effect of solvent hydration on the extraction of linalool, Arce et al. [18] reported a similar observation, showing that a higher level of linalool extraction is achieved when a lower level of water is used.

Figure 2 shows that the increase of linalool in the overall composition also resulted in lower migration of linalool and higher migration of limonene from the terpene to the solvent phase. This effect was also observed by other authors in different systems [13, 18, 25, 29, 39, 40, 44], in which the increase of the content of oxygenated compounds (linalool, carvone or citral, respectively) leads to the increase in phase solubility. As a consequence, the migration of linalool from the terpene to the solvent phase is reduced, while the extraction of limonene is increased.



**Fig. 2** - Equilibrium diagrams for the model systems composed of limonene (1), linalool (2), ethanol (3) and water (4), at  $(298.2 \pm 0.1)$  K. Calculated by correlation procedure: - - -, NRTL model; ·····, UNIQUAC model. (a)  $w_{4S} = 0.235 \pm 0.002$ ; (b)  $w_{4S} = 0.318 \pm 0.004$ ; (c)  $w_{4S} = 0.412 \pm 0.003$ .

Ternary mixtures composed of limonene, ethanol and water available in the NIST Data Archive [11, 29] were compared with the baselines of the diagrams, and a very good agreement was observed in terms of inclination and length of tie lines (data not shown).

Relative to quaternary mixtures composed of limonene, linalool, ethanol and water, data previously reported by Arce et al. [18] demonstrate that, from a qualitative point of view, the results obtained in this work are in agreement with results reported by Arce et al. [18], especially in relation to the effect of the amount of linalool and solvent hydration on the oxygenated compound extraction. However, the data published by Arce et al. [18] were determined using a thermal conductivity detector in the chromatographic analysis while the data shown in this manuscript were determined using a flame ionization detector, and this difference in detectors can result in differences from the quantitative point of view. Advantages of the FID include a detection limit that is approximately two to three orders of magnitude lower than the detection limit for a thermal conductivity detector, and a linear response over  $10^6$ – $10^7$  times the amount of analyte injected.

The LLE experimental data set was used to adjust new binary interaction parameters of the NRTL and UNIQUAC thermodynamic models, with the results shown in Table 6. The mean standard deviation related to the correlation process, calculated by Eq. (5), is exhibited in Table 5. In Figure 2, the thermodynamic models provided satisfactory representations of the phase compositions of the model systems, because low values of mean deviation were obtained (Table 5).

In general, compared with the NRTL model, the UNIQUAC model parameters better describe the phase compositions. However, for the ethanol system with a 0.235 mass fraction of water content (Figure 2a), the NRTL model was unable to calculate the composition of the tie line, which represented the 0.1500 mass fraction of linalool in the overall composition, possibly due to the high solubility of the compounds in this tie line.

#### **I.3.4. Prediction of the phase compositions of the real systems using new NRTL and UNIQUAC parameters**

Figure 3 presents solvent selectivity and the distribution coefficients for the essential oil pseudo-compounds [terpene fraction (1) and oxygenated fraction (2)] present in the real systems composed of COEO and hydroalcoholic solvents, as a function of essential oil/ solvent mass ratio.

The distribution coefficient ( $k_i$ ), calculated according to Eq. (8), represents the migration of a specific compound from the terpene-rich (TP) to the solvent-rich (SP) phase. The solvent selectivity ( $S_{2/1}$ ), calculated by Eq. (9), represents the capacity of the solvent to separate the oxygenated compounds from the terpenes.

$$k_i = \frac{w_{i,SP}}{w_{i,TP}} \quad (8)$$

where  $w_{i,SP}$  and  $w_{i,TP}$  are the mass fractions of the pseudo-component  $i$  (terpenes or oxygenated compounds) in the SP and the TP, respectively.

$$S_{2/1} = \frac{k_2}{k_1} \quad (9)$$

where  $k_2$  is the distribution coefficient of oxygenated compounds, and  $k_1$  is the distribution coefficient of terpenes.

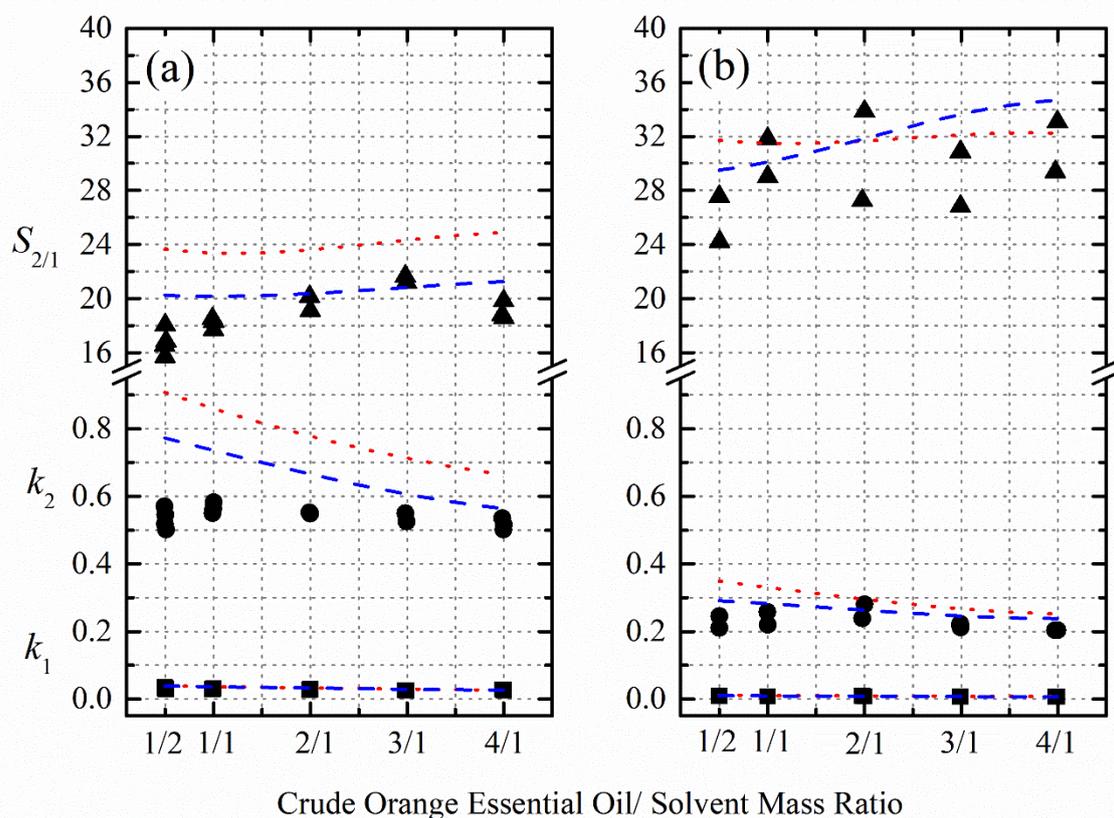
The increasing amount of water in the solvent causes a decrease in the values of  $k_1$  and  $k_2$ , which indicates lower migration of the compounds from the terpene-rich to solvent-rich phase.

Figure 3 shows that  $k_2$  values are significantly larger than  $k_1$  values. The greater the difference between  $k_1$  and  $k_2$ , the better the liquid–liquid extraction separation between the oxygenated compounds and the terpene compounds.

Because the  $k_2$  values are greater than  $k_1$ , the  $S_{2/1}$  values are greater than 1.0, which indicates that the solvents are more selective for oxygenated compounds than for terpene compounds, independent of their hydration level. Although the increase of water content in the solvent leads to lower  $k_i$  values, a higher  $S_{2/1}$  indicates higher water content, as observed in the reduced phase solubility in the presence of water in the system, as previously reported in several studies in which ethanol and water mixtures were used as solvents [28, 29, 31, 39, 40, 44].

Calculated values of solvent selectivity and distribution coefficients, estimated using the new interaction parameters proposed by this work, are also shown in Figure 3. The new interaction parameters of NRTL and UNIQUAC models, shown in Table 6, provided satisfactory representations of  $k_1$ ,  $k_2$  and  $S_{2/1}$  values. The performance of this new set of parameters is also shown in Figures 1c and 1d, in comparison with parameters from Arce et al. [18] (Figures 1a and 1b). The new parameters are able to describe the phase splitting and the partition of linalool between the phases. The good performance of the models is corroborated by the low mean deviations (Table 5) for this prediction process.

Based on the mean deviation values shown in Table 5, in relation to the NRTL model, the new set of parameters allows a significant gain in the quality of the description of composition because the deviation in the mass fraction decreased from 0.2098 to 0.0031. Regarding the UNIQUAC model, the gain is also important. The gain in the mass fraction decreases from 0.0476 to 0.0027 with the new set of parameters versus those proposed by Arce et al. [18].



**Fig. 3** - Distribution coefficients of essential oil compounds ( $k_i$ ) and selectivity ( $S_{2/1}$ ), at  $(298.2 \pm 0.1)$  K, for the real systems composed of crude orange essential oil (COEO), represented by terpenes (1), oxygenated compounds (2), ethanol (3) and water (4). Experimental:  $\blacksquare$ ,  $k_1$ ;  $\bullet$ ,  $k_2$ ;  $\blacktriangle$ ,  $S_{2/1}$ . Calculated by prediction procedure using the new parameters from Table 6:  $---$ , NRTL model;  $\cdots$ , UNIQUAC model. (a)  $w_{4S} = 0.295 \pm 0.005$ ; (b)  $w_{4S} = 0.415 \pm 0.007$ .

#### **I.4. Conclusions**

The presence of water in the alcoholic solvents caused changes in the extraction efficiency and in the technological feasibility of the deterpenation process of citrus essential oil by liquid–liquid extraction. The extraction of the terpene and the oxygenated fractions was affected by an increased alcoholic solvent hydration level that resulted in higher values of solvent selectivity.

The new binary interaction parameters for NRTL and UNIQUAC thermodynamic models accurately described the phase compositions for the citrus model systems investigated. The results obtained for the prediction of liquid–liquid equilibrium for real systems composed of crude orange essential oil showed that the strategy of constructing model systems for parameter adjustment was valid despite the differences between the systems. These results confirm that the approach considering the real systems composed by pseudo-compounds can be used in this type of system, providing a good prediction of the phase compositions for the real systems, which are more complex systems, composed of several components. These results show that these parameters can be useful in the study of the fractionation of crude oils by liquid–liquid extraction using computational simulations.

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## CHAPTER II: Effect of *Citrus sinensis* essential oil deterpenation on the aroma profile of the phases obtained by solvent extraction

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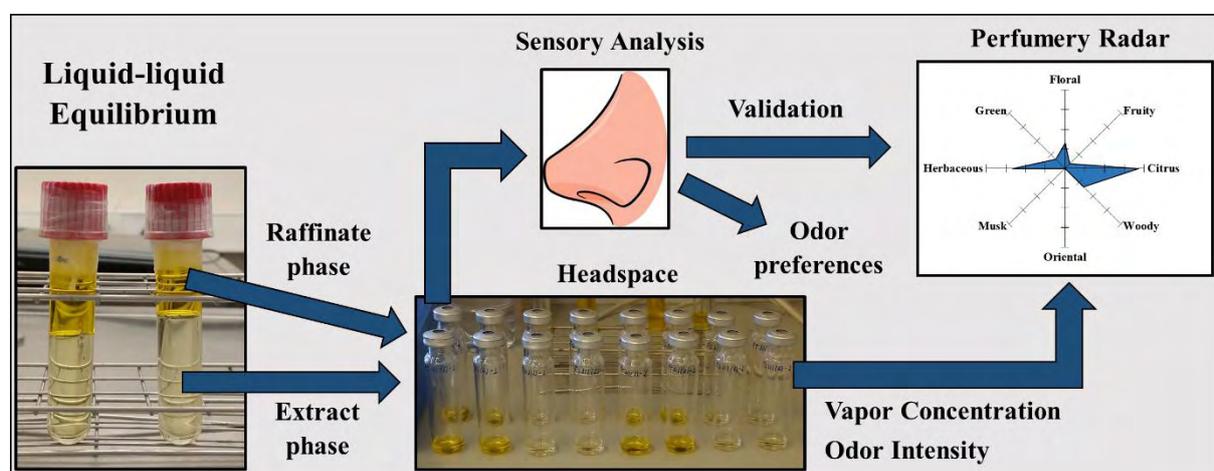
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### II. Graphical Abstract



### II. Highlights

- Crude orange EO was fractionated using ethanol/water mixtures as solvents.
- Odor intensities were estimated by the Stevens' power law concept.
- LLE phases were more citrus and herbaceous than the crude orange essential oil.
- The fractionation process did not affect the orange essential oil original aroma.
- The extract phases exhibited the most valued sensory qualities.

## II. Abstract

The aroma profile of crude *Citrus sinensis* essential oil (EO) and its phases from the fractionation process by solvent extraction were evaluated. Ethanol with 30 and 40 (%w/w) water were prepared as solvents, and different mass ratios between EO and the solvent (EO/S = 4/1, 1/1, and 1/2) were used to reach the liquid-liquid equilibrium (LLE). The concentration of the components in the vapor phase above the liquid mixtures (crude EO and LLE phases) were experimentally assessed by headspace analysis. The odor intensity of each component was estimated by Stevens' power law concept and classified into olfactory families using the Perfumery Radar procedure. LLE phases, crude and a model orange EO were evaluated in a brief sensory analysis. The extract phase obtained using ethanol with 40 (%w/w) water as solvent and EO/S 1/1 exhibited the most valued sensory and chemical characteristics. The solvent extraction was an efficient technique to yield extract phases with aroma resembling the crude orange EO, which may be incorporated into aqueous products, such as perfumes and beverages.

Keywords: liquid–liquid equilibrium; headspace; ethanol; odour intensity; perfumery radar

## II.1. Introduction

*Citrus sinensis* (L.) Osbeck (orange) is the most cultivated citrus species in the world, representing almost 25% of the global flavor market, and being one of the most used flavors in beverages [1–3]. Citrus essential oils (EOs), usually extracted from the peel of citrus fruits, are appreciated by different industries due to their pleasant aroma, and they have an incredible array of applications: in the food industry, they are incorporated in many food products as flavoring agents (e.g., soft drinks, ice creams, or candies); in the chemical industry, they are used as fragrances in air fresheners and cleaning products; and in the perfume industry, they are used as primary raw materials for the formulation of toiletries and perfumes [4–6]. The typical aroma of the orange EO results from a complex mixture of different components [2]. Monoterpene hydrocarbons are the primary constituents of the EO from the orange peel, with limonene as the most abundant compound [90 – 98 (%w/w)] [7,8]. Interestingly, although limonene comprises more than 90 (%w/w) of the volatile composition of the EO, its contribution to the final aroma of the mixture is limited [2] by its instability and the possibility of formation of off-flavor compounds [9,10]. For instance, existing data in the literature highlight minor volatile components, such as linalool, octanal, citronellal, and other oxygenated compounds as the main responsible ones for the characteristic aroma of the orange peel EO [1]. As observed in many other fruits, the aroma of fresh orange is mostly attributed to aldehydes and esters, in addition to some alcohols, ketones, and lastly to hydrocarbon terpenes [11].

As mentioned above, the demand for the aroma of orange EO is huge and, because of this, it is of prime interest that its particular sensory quality is maintained. However, terpene hydrocarbons are susceptible to degradation reactions when exposed to air, light, and heat, generating unpleasant compounds [9,10,12]. This degradation process negatively affects the sensory quality of the orange EO and, consequently, its market price [9]. Vacuum distillation is the most usual industrial process applied for the orange EO deterpenation; however, some problems associated with the boiling points of the components, vacuum control, start-up, and process stabilization have been reported [13]. Hence, alternative methods have been proposed aiming at improving the sensory quality and stability of citrus EOs. Taylor and Linforth [14] point out that solvent extraction, compared to the usual distillation process, may generate a product with better quality of aroma, since this process generally retains the most volatile components, which are responsible for the typical aroma of citrus EO. Moreover, the heat used in distillation processes is possibly associated with the loss of more volatile components and changes in the original aroma of the crude citrus EO [14]. Solvent extraction using ethanol and

water mixtures as solvents have recently been applied to separate terpenes and oxygenated compounds from mixtures containing key components of lemon (limonene,  $\gamma$ -terpinene,  $\beta$ -pinene, and citral) [15], bergamot (limonene, linalyl acetate, and linalool) [16], and orange OEs [9,17]. These hydroalcoholic solvents have also been employed in the fractionation of crude EOs, such as orange [9], bergamot [12], and acid lime [10]. Ethanol is classified as solvent class 3 by FDA [18], which means low toxic and low risk to human health, allowing its use in food formulations. Additionally, ethanol is an eco-friendly solvent [19] with low cost [20], being bio-renewable and available in a natural form [21].

*C. sinensis* Valencia and Pera Rio varieties have been studied due to their economic relevance; they are the main orange varieties produced in Brazil, which is the main producer and exporter of orange EOs [22]. Recently, Gonçalves et al. [9] reported the chemical behavior of systems composed of crude *C. sinensis* EO (mixture of Valencia and Pera Rio varieties) and ethanol/water mixtures, at  $298.2 \pm 0.1$  K. The authors studied the liquid-liquid equilibrium (LLE) in terms of partition coefficient of terpenes and oxygenated compounds, and solvent selectivity. They found that the water content in the solvent and the amount of oxygenated compounds in the mixture influenced the distribution of the components and solvent selectivity.

Curiously, although fractionation of citrus EOs is reported as a process that may improve the sensorial characteristics of these oils [6,9,12,14,15,23,24], studies demonstrating the real impact of this procedure on their aroma are rare. Recently, Gonçalves et al. [10] reported the aroma profile evaluation of the phases from the acid lime EO fractionation using ethanol and water mixtures. The authors found that the process does not affect strongly the typical acid lime EO aroma, independently of the water content in the solvent.

Although the deterpenation process of orange EO using ethanol/water mixtures was already conducted by Gonçalves et al. [9], the impact of the process on the aroma of the phases remains unknown. Therefore, for the first time, the aroma profile of each LLE phase (raffinate and extract) of the systems composed of crude orange EO and solvent (ethanol and water mixtures) was investigated and compared to the original orange EO aroma. In order to achieve this aim, systems containing different ratios of EO and solvent (EO/S = 4/1, 1/1 and 1/2), and two different concentrations of water in the solvent [30 and 40 (% w/w)] were prepared. The liquid crude orange EO and the LLE phases were chemically characterized, and the concentration of the components in the respective vapor phases was assessed by headspace analysis. After that, the odor intensity of each component was estimated using the Stevens' power law ( $\Psi_i$ ) concept [25], which was used in the construction of Perfumery Radars (PRs) [26]. Finally, a brief

sensory evaluation was conducted aiming at the validation of the headspace analysis and the PRs.

## **II.2. Material and methods**

### **II.2.1. Materials**

*C. sinensis* EO was industrially extracted from the peels of Valencia and Pera Rio varieties by cold pressing. The EO was donated by Louis Dreyfus Company (Brazil). Solvents were prepared by diluting absolute ethanol with deionized water. The water mass percentages (%w/w) in the solvents were:  $30.0 \pm 0.5$ , and  $42.5 \pm 0.7$ . Medicinal air, helium, hydrogen, and synthetic air were acquired from Air Liquide (Portugal). The empirical formulas, molar masses, CAS registry numbers, source and supplier purities, experimental purities, vapor pressures, odor detection thresholds in air, power law exponents, and the classification into the olfactory families of each studied component are displayed in Table 1. The crude orange EO experimental composition, vapor concentrations, and odor intensities of the components identified in the EO are also shown in Table 1.

**Table 1:** Empirical formulas, molar masses ( $M_i$ , in  $\text{g}\cdot\text{mol}^{-1}$ ), vapor pressures ( $P_i^{sat}$ , in Pa), odor detection thresholds in air ( $ODT_i$ , in  $\text{g}\cdot\text{m}^{-3}$ ), power law exponent ( $n_i$ ), olfactory family classification of each component, experimental composition ( $w_i$ , in mass percentage), vapor concentration ( $C_i^v$ , in  $\text{g}\cdot\text{m}^{-3}$ ), and odor intensities ( $\Psi_i$ ) of the components identified in crude orange essential oil at the temperature  $T = 298.2$  K and pressure  $p = 1.02 \times 10^5$  Pa<sup>a</sup>

Component ( <i>i</i> )	Empirical Formula	$M_i$ ( $\text{g}\cdot\text{mol}^{-1}$ )	CAS number	Source and supplier purity	GC purity <sup>b</sup>	$P_i^{sat}$ (Pa)	$ODT_i$ ( $\text{g}\cdot\text{m}^{-3}$ ) <sup>c</sup>	$n_i^d$	Olfactory Family <sup>e</sup>		Crude Orange Essential Oil		
									Primary	Secondary	% $w_i$	$C_i^v$ ( $\text{g}\cdot\text{m}^{-3}$ )	$\Psi_i$
Ethanol	C <sub>2</sub> H <sub>6</sub> O	46.07	64-17-5	Chem-Lab, Belgium, ≥99.8%	99.9%	7901 <sup>f</sup>	3.74×10 <sup>-2</sup>	0.58	Alcohol				
Water	H <sub>2</sub> O	18.02	7732-18-5				3172 <sup>f</sup>			Odorless			
<i>Terpenes</i>		136.2									98.4 ± 0.1	20.8 ± 0.7	113 ± 4
<i>α</i> -Pinene	C <sub>10</sub> H <sub>16</sub>	136.2	7785-26-4	Sigma-Aldrich, USA, 98%	99.0%	633.3 <sup>f</sup>	2.88×10 <sup>-4</sup>	0.49	Herbaceous	Woody	2.4 ± 0.1	1.43 ± 0.04	65 ± 2
Limonene	C <sub>10</sub> H <sub>16</sub>	136.2	5989-27-5	Sigma-Aldrich, USA, 97%	98.8%	206.4 <sup>f</sup>	5.60×10 <sup>-4</sup>	0.37	Citrus		96.1 ± 0.1	19.4 ± 0.7	48 ± 2
<i>Oxygenated</i>		146.6									1.6 ± 0.1	0.123 ± 0.005	58 ± 2
Octanal	C <sub>8</sub> H <sub>18</sub> O	128.2	124-13-0	Sigma-Aldrich, USA, ≥92%	92.0%	157.3 <sup>h</sup>	1.46×10 <sup>-5</sup>	0.33	Green	Fruity	0.4 ± 0.1	0.067 ± 0.002	16.1 ± 0.5
Octanol	C <sub>8</sub> H <sub>18</sub> O	130.2	111-87-5	Acros, Germany, 99%	99.0%	10.59 <sup>g</sup>	1.11×10 <sup>-4</sup>	0.29	Floral	Fruity	0.1 ± 0.1	0.006 ± 0.001	3.1 ± 0.2
Nonanal	C <sub>9</sub> H <sub>18</sub> O	142.2	124-19-6	TCI, Japan, >95%	95.0%	49.33 <sup>f</sup>	5.92×10 <sup>-5</sup>	0.34	Floral	Citrus	<i>t</i>	0.009 ± 0.001	5.6 ± 0.1
Neral	C <sub>10</sub> H <sub>16</sub> O	152.2	5392-40-5	Sigma-Aldrich, USA, 96%	99.0%	12.17 <sup>g</sup>	3.62×10 <sup>-5</sup>	0.32	Floral	Citrus	<i>t</i>	0.003 ± 0.001	4.20 ± 0.08
Geranial	C <sub>10</sub> H <sub>16</sub> O	152.2	5392-40-5	Sigma-Aldrich, USA, 96%	99.0%	12.17 <sup>g</sup>	4.00×10 <sup>-5</sup>	0.31	Floral	Citrus	0.1 ± 0.1	0.002 ± 0.001	3.4 ± 0.5
Citronellal	C <sub>10</sub> H <sub>18</sub> O	154.3	106-23-0	Sigma-Aldrich, USA, ≥95%	99.0%	37.33 <sup>g</sup>	2.94×10 <sup>-5*</sup>	0.36	Citrus	Woody	0.3 ± 0.1	0.017 ± 0.001	9.80 ± 0.06
Linalool	C <sub>10</sub> H <sub>18</sub> O	154.3	78-70-6	Sigma-Aldrich, USA, 97%	99.2%	21.33 <sup>f</sup>	1.73×10 <sup>-5</sup>	0.35	Floral	Citrus	0.5 ± 0.1	0.027 ± 0.001	13.1 ± 0.5
<i>α</i> -Terpineol	C <sub>10</sub> H <sub>18</sub> O	154.3	98-55-5	Sigma-Aldrich, USA, 90%	92.0%	5.640 <sup>f</sup>	1.09×10 <sup>-4</sup>	0.35 <sup>i</sup>	Floral	Citrus	0.1 ± 0.1	0.002 ± 0.001	2.4 ± 0.2
Undecanal	C <sub>11</sub> H <sub>22</sub> O	170.3	112-44-7	Sigma-Aldrich, USA, 97%	97.0%	11.09 <sup>g</sup>	1.40×10 <sup>-4</sup>	0.39	Citrus	Fruity	<i>t</i>		
Dodecanal	C <sub>12</sub> H <sub>24</sub> O	184.3	112-54-9	Sigma-Aldrich, USA, 92%	92.0%	2.040 <sup>f</sup>	3.30×10 <sup>-5</sup>	0.35 <sup>i</sup>	Floral	Citrus	<i>t</i>		

<sup>a</sup> Standard uncertainties  $u$  are  $u(T) = 0.1$  K,  $u(p) = 1 \times 10^3$  Pa,  $u(\%w_i)$  presented after the mass percentage value,  $u(C_i^v)$  after the vapor concentration value, and  $u(\Psi_i)$  after the odor intensity value;

<sup>b</sup> Experimentally determined by GC-FID analysis without further purification, given as mass percentage;

<sup>c</sup> Geometric averages from van Gemert [29] database;

<sup>d</sup> From Devos et al. [33];

<sup>e</sup> Classified according to the descriptions from Brechbill [34], CAMEO Chemicals [35], Parchem [36], and The Good Scents Company [37];

<sup>f</sup> Experimental values from SRC HysProp Database [45];

<sup>g</sup> Estimated values from NCBI PubChem Database, by Antoine equation [46];

<sup>h</sup> Extrapolated value from SRC HysProp Database [45];

<sup>i</sup> The median power law exponent value in the compilation of data from Devos et al. [33];

\* Geometrically averaged from Padrayuttawat et al. [31] and experimental value evaluated in this study ( $2.88 \times 10^{-5}$   $\text{g}\cdot\text{m}^{-3}$ );

*t* Mass percentage lower than 0.1%.

## **II.2.2. Liquid–liquid and vapor–liquid equilibria**

The effect of water on the odor profile of the fractionated EO (phases from the LLE) was appraised using ethanol with 30 and 40 (%w/w) water as solvents. In addition, three different mass ratios between EO and the solvent (EO/S), already studied by Gonçalves et al. [9], were prepared aiming at the evaluation of the effect of solvent content in the system on the odor profile of the mixtures. LLE systems were prepared and samples were separately collected according to the procedure previously described by Gonçalves et al. [9] for the crude orange EO. The vapor–liquid equilibrium and headspace analysis of the crude EO, raffinate and extract phases were conducted as defined by Gonçalves et al. [10].

Type A standard uncertainty [27] was estimated to be less than or equal to 0.001 [or 0.1 (%w)] for the mass fractions in the liquid phases and  $0.001 \text{ g}\cdot\text{m}^{-3}$  for the vapor concentrations.

## **II.2.3. Chemical analyses**

### **II.2.3.1. Liquid phase**

The chemical characterization of the volatile components in the crude liquid orange EO and the phases from the LLE was performed in a gas chromatograph (GC) according to Gonçalves et al. [10] using a Varian CP-3800 equipped with a split/splitless injector coupled to mass spectrometry (MS), and a capillary column DB-FFAP (Agilent, USA) (0.25  $\mu\text{m}$  film thickness, 30 m  $\times$  0.25 mm i.d.). All the GC-MS analysis conditions were the same as described by Gonçalves et al. [9,10]. The components were identified by similarity with mass spectral libraries (NIST98, USA, and the mass spectral database of Flavors and Fragrances of Natural and Synthetic Compounds 2, USA), and by comparison with the retention times of standards. The components were quantified in a Varian CP-3800 equipped with a split/splitless injector, flame ionization detector (FID), under the same GC-MS analysis conditions. The carrier gas was maintained at a constant flow rate of  $1.13 \text{ mL}\cdot\text{min}^{-1}$  and the detector was maintained at 523.2 K. The quantification of the components was done by an external standard method, and all the analyses were conducted in duplicate.

### **II.2.3.2. Vapor phases**

Experimental concentrations in the vapor phase above the liquid mixtures were determined in a static headspace gas chromatograph (HS-GC) using a Varian CP-3800 equipped with a split/splitless injector, flame ionization detector (FID), and a capillary column DB-FFAP

(Agilent, USA) (0.25  $\mu\text{m}$  film thickness, 30 m  $\times$  0.25 mm i.d.), according to method adopted by Gonçalves et al. [10]. Vapor samples (0.2 mL) were injected using a split ratio of 50/1 for the crude EO and raffinate phases, and 150/1 for the extract phases. Vapor sampling and injection were performed using a gas-tight syringe (SGE, Australia) installed in an automatic headspace sampler HT250D (HTA s.r.l., Italy). The carrier gas, oven temperature program, injector temperature, and FID temperature were the same used for the analysis of the liquid phases (section 2.3.1). The quantification of the components was performed by external standard method. The HS-GC assays were carried out in triplicate.

#### II.2.4. Odor Intensity

The odor intensities of the components identified in the orange EO and in the LLE phases were estimated using the psychophysical Stevens' power law concept ( $\Psi_i$ ) [25]. This model enables the valuation of the odor strength of an odorant present in a mixture, and is described by the ratio between the concentration of the component  $i$  in the vapor phase (headspace) ( $C_i^v$ , in  $\text{g}\cdot\text{m}^{-3}$ ) and its odor detection threshold in the air ( $ODT_i$ , in  $\text{g}\cdot\text{m}^{-3}$ ), raised to its power law exponent ( $n_i$ ) [Eq (1)].

$$\Psi_i = \left( \frac{C_i^v}{ODT_i} \right)^{n_i} \quad (1)$$

$ODT_i$  is the minimum concentration of an odorant  $i$  detectable by the human nose in the air, water or other media [28]. In this study,  $ODT$ s values shown in Table 1, used for the determination of  $\Psi_i$ , were geometrically averaged from van Gemert database [29], which is a recommended procedure commonly applied in sensory analysis [30]. For the particular case of citronellal, which is an important component present in the crude orange EO, only one  $ODT$  value was reported in the literature, as far as we know [31]. Due to this fact, the  $ODT$  of citronellal was experimentally measured in this study according to Gomes et al. [32] and described in the section 2.4.1. The  $n_i$  values were collected from Devos et al. [33] database. For the components that the  $n_i$  values were not found, such as  $\alpha$ -terpineol and dodecanal, the median power law exponent 0.35 was used [33], as demonstrated in Table 1.

##### II.2.4.1. Odor detection threshold measurement

The measurement of the  $ODT$  for citronellal in the air was performed according to Gomes et al. [32] and also implemented in prior analysis [10] using an Ecoma olfactometer (model

T07, Germany), built according to VDI3881 (1980) and EN13725 (2003) standards. The gas sample was prepared in a 5 L Nanoplan NA gas sampling bag (Olfasense, Germany) with a PET tube that was used to supply the sample to the olfactometer. To this purpose, a known gas volume of the pure component was diluted in medicinal air inside the bag and the gas mixture was maintained static for 1 h at  $298.2 \pm 0.1$  K before the analysis. The measurements were carried out by a panel constituted by eight untrained people belonging to the laboratory, four women and four men, 27 and 32 years old, at controlled room temperature of  $298 \pm 1$  K. The experimental conditions for the measurements were the same used in previous assays [10], as suggested by Gomes et al. [32]. The odor detection threshold of citronellal in the air ( $ODT$ , in  $\text{g}\cdot\text{m}^{-3}$ ) was calculated by Eq. (2).

$$ODT = \frac{C^0}{10^M} \quad (2)$$

where  $C^0$  is the gas concentration of citronellal inside the sampling bag (in  $\text{g}\cdot\text{m}^{-3}$ ) and  $M$  is the arithmetic average of the logarithms of all threshold dilution factors, calculated by Eq. (3).

$$M = \frac{\sum_{k=1}^8 \sum_{l=1}^3 \log_{10}(Z_{k,l}^{thr})}{L} \quad (3)$$

where  $Z_{k,l}^{thr}$  [Eq. (4)] is the threshold dilution factor for panelist  $k$  at a measuring sequence  $l$ , and  $L$  is the total number of answers.

$$Z_{k,l}^{thr} = \sqrt{Z_N \cdot Z_{N-1}} \quad (4)$$

where  $Z_N$  is the dilution of the first positive answer, while  $Z_{N-1}$  is the dilution of the last negative answer (when no odor was detected). The calculation was performed after obtaining two consecutive positive answers ( $Z_N$  and  $Z_{N+1}$ ) (when some odor was detected). The geometrical average between the  $ODT$  of citronellal from the literature [31], and the value determined in this analysis ( $2.88 \times 10^{-5} \text{ g}\cdot\text{m}^{-3}$ ), together with the  $ODT$  of all components is displayed in Table 1.

## II.2.5. Classification of the orange EO and the LLE phases into the olfactory families

The crude orange EO and the LLE phases were classified into olfactory families using a methodology called Perfumery Radar (PR), developed by Teixeira et al. [26]. The PR is an efficient tool for the classification of a mixture into olfactory qualities. This approach considers that the overall scent of a fragrance mixture is governed by a single odorant with a distinctive

stronger sensation [26,28]. Gonçalves et al. [10] adopted this tool to characterize the aroma profile of the crude acid lime EO and the phases from its fractionation. Similarly, in this study, the PRs were constructed using the estimated odor intensities of the components [Eq. (3)] assessed by headspace analysis. Therefore, each component identified and quantified in the vapor phases was classified into olfactory families according to the literature [34] and aroma supplier descriptions [35–37] (Table 1). Since the same compound may be classified in more than one olfactory family [26], the primary and secondary families of each component were considered. Finally, the PRs of the samples were compared to the sensory description, as explained in the following section.

### II.2.6. Sensory analysis

Sensory analysis was carried out with three purposes: (i) to compare the classification in olfactory families obtained by the PR methodology with the sensibility of the human nose; (ii) to validate the headspace analysis; and (iii) to investigate the preference of the panelists between the raffinate or extract phases, in terms of sensory qualities. The panel was composed of seven panelists (four women and three men, untrained, 24 - 33 years old, from the laboratory). Based on the PR constructed for the crude orange EO (Fig. 1a), four aroma standards were selected to represent each primary olfactory family (Table 1): limonene (citrus),  $\alpha$ -pinene (herbaceous), octanal (green), and linalool (floral). First, the aroma standards were presented to the panelists and their odor descriptions were discussed by them. Then, panelists were invited to identify the primary families represented by each aroma standard. After this brief training, the crude EO and the LLE phases were analyzed during four formal sessions. The panelists classified the samples into the main olfactory families using a scale from 4 (most evident) to 1 (less evident). Samples were presented in a random order and the aroma standards were smelled as necessary by the panelists during each section. In order to validate the headspace analysis, a model mixture of pure components simulating the composition of the crude EO was prepared taking into account the compounds identified in the headspace analysis and following the experimental liquid concentrations shown in Table 1. This mixture was also presented to the panelists and its aroma was compared to the real orange EO. Finally, the panelists were invited, as final consumers, to select among raffinate and extract phases the sample with the most pleasant aroma resembling the original orange EO aroma.

## II.2.7. Statistical Analysis

The differences among the PR constructed for the crude EO and the LLE phases, in terms of olfactory families, were evaluated by variance analysis with Duncan's [38] test at a significance level of  $P \leq 0.05$ , using SAS® software (version 9.2, SAS Institute Inc., USA).

## II.3. Results and discussion

### II.3.1. Experimental compositions of crude orange essential oil and phases from the liquid–liquid equilibrium

The composition of the crude liquid orange EO (%w<sub>i</sub>), vapor concentration ( $C_i^v$ , in g·m<sup>-3</sup>), and odor intensity of each component ( $\Psi_i$ ) are presented in Table 1. The chemical analysis revealed that monoterpenes [ $98.4 \pm 0.1$  (%w/w)] were the main group of volatile components found in the crude EO, followed by oxygenated compounds [ $1.6 \pm 0.1$  (%w/w)] (Table 1). Limonene was the major component identified, comprising  $96.1 \pm 0.1$  (%w/w) of the volatile fraction of the orange EO. The remaining 4.0 (%w/w) was a complex mixture of  $\alpha$ -pinene ( $2.4 \pm 0.1$ ) and oxygenated compounds, such as linalool ( $0.5 \pm 0.1$ ), octanal ( $0.4 \pm 0.1$ ), citronellal ( $0.3 \pm 0.1$ ), octanol ( $0.1 \pm 0.1$ ), geranial ( $0.1 \pm 0.1$ ),  $\alpha$ -terpineol ( $0.1 \pm 0.1$ ) (%w/w), and other components detected at lower mass percentages (nonanal, neral, dodecanal, and undecanal). These results are aligned with a previous study by Gonçalves et al. [9] for the same orange EO (mixture of Valencia and Pera Rio varieties), but from a different batch.

Concerning the chemical composition of the LLE phases (Table 2), the raffinate phases were rich in monoterpenes (limonene and  $\alpha$ -pinene), and the extract phases were rich in solvent (ethanol and water). Overall, the increment in the amount of solvent in the system (EO/S from 4/1 to 1/2) increased the migration of all components from the raffinate phase to the extract phase. The increased water content in the solvent, from 30 to 40 (%w/w) caused more retention of the components in the raffinate phases, mainly terpenes. The migration of the oxygenated compounds from the raffinate to the extract phase was greater than the one of terpenes. This means that the solvent has higher selectivity for these components than for terpenes, as already verified and discussed by Gonçalves et al. [9].

**Table 2:** Experimental liquid–liquid equilibrium data for systems composed of crude orange essential oil, represented by terpenes + oxygenated compounds + ethanol + water, in mass percentages (%w), at the temperature  $T = 298.2$  K and pressure  $p = 1.02 \times 10^5$  Pa<sup>a</sup>, for solvents 30 and 40 (%w/w) water, and different essential oil to solvent mass ratios (EO/S).

Component ( <i>i</i> )	Solvent 30 (%w/w) water			Solvent 40 (%w/w) water		
	EO/S = 4/1	EO/S = 1/1	EO/S = 1/2	EO/S = 4/1	EO/S = 1/1	EO/S = 1/2
<i>Raffinate Phases</i>						
<i>Terpenes</i>	95.1 ± 0.1	95.5 ± 0.1	95.9 ± 0.1	96.0 ± 0.1	96.0 ± 0.1	96.4 ± 0.2
α-Pinene	2.3 ± 0.1	2.2 ± 0.1	2.3 ± 0.1	2.3 ± 0.1	2.3 ± 0.1	2.3 ± 0.1
Limonene	92.8 ± 0.1	93.2 ± 0.1	93.7 ± 0.1	93.7 ± 0.1	93.7 ± 0.1	94.1 ± 0.3
<i>Oxygenated</i>	1.4 ± 0.1	1.0 ± 0.1	0.7 ± 0.1	1.5 ± 0.1	1.1 ± 0.2	1.0 ± 0.1
Octanal	0.3 ± 0.1	0.2 ± 0.1	0.2 ± 0.1	0.4 ± 0.1	0.3 ± 0.1	0.3 ± 0.1
Octanol	0.1 ± 0.1	<i>t</i>	<i>t</i>	0.1 ± 0.1	<i>t</i>	<i>t</i>
Nonanal	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>
Neral	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>
Geranial	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1
Citronellal	0.3 ± 0.1	0.2 ± 0.1	0.2 ± 0.1	0.3 ± 0.1	0.3 ± 0.1	0.2 ± 0.1
Linalool	0.4 ± 0.1	0.3 ± 0.1	0.2 ± 0.1	0.5 ± 0.1	0.3 ± 0.1	0.3 ± 0.1
α-Terpineol	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>
Undecanal	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>
Dodecanal	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>
<i>Solvent</i>	3.5 ± 0.1	3.5 ± 0.1	3.3 ± 0.1	2.6 ± 0.1	2.9 ± 0.2	2.6 ± 0.2
Ethanol	3.2 ± 0.1	3.3 ± 0.1	3.1 ± 0.2	2.4 ± 0.1	2.7 ± 0.2	2.3 ± 0.1
Water	0.22 ± 0.01	0.2 ± 0.1	0.2 ± 0.1	0.2 ± 0.1	0.2 ± 0.1	0.2 ± 0.1
<i>Extract Phases</i>						
<i>Terpenes</i>	2.6 ± 0.1	3.0 ± 0.1	3.2 ± 0.2	0.6 ± 0.1	1.2 ± 0.6	0.8 ± 0.1
α-Pinene	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	<i>t</i>	<i>t</i>	<i>t</i>
Limonene	2.5 ± 0.2	2.9 ± 0.1	3.1 ± 0.2	0.6 ± 0.1	1.1 ± 0.6	0.8 ± 0.1
<i>Oxygenated</i>	0.7 ± 0.1	0.5 ± 0.1	0.4 ± 0.1	0.3 ± 0.1	0.3 ± 0.1	0.2 ± 0.1
Octanal	0.2 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	<i>t</i>
Octanol	0.1 ± 0.1	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>
Nonanal	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>
Neral	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>
Geranial	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>
Citronellal	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	<i>t</i>	<i>t</i>	<i>t</i>
Linalool	0.3 ± 0.1	0.2 ± 0.1	0.2 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1
α-Terpineol	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>
Undecanal	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>
Dodecanal	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>	<i>t</i>
<i>Solvent</i>	96.7 ± 0.2	96.5 ± 0.1	96.5 ± 0.2	99.1 ± 0.1	98.5 ± 0.7	98.9 ± 0.1
Ethanol	64 ± 1	67.0 ± 0.3	67.5 ± 0.4	53.6 ± 0.4	56.1 ± 0.5	57 ± 1
Water	33 ± 1	29.5 ± 0.3	29.0 ± 0.4	45.4 ± 0.3	42 ± 1	42 ± 1

<sup>a</sup> Standard uncertainties  $u$  are  $u(T) = 0.1$  K,  $u(p) = 1 \times 10^3$  Pa, and  $u(\%w)$  presented after each mass percentage value;

*t* Mass percentage lower than 0.1%.

## II.3.2. Vapor phases

### II.3.2.1. Crude orange essential oil

The concentrations of the components in the vapor phases ( $C_i^v$ , in  $\text{g}\cdot\text{m}^{-3}$ ) were experimentally determined by HS-GC. The terpenes limonene and  $\alpha$ -pinene were the major component quantified in both liquid [ $96.1 \pm 0.1$ , and  $2.4 \pm 0.1$  (%w/w)], respectively] and vapor phases ( $19.4 \pm 0.7$ , and  $1.43 \pm 0.04$   $\text{g}\cdot\text{m}^{-3}$ , respectively) (Table 1). The oxygenated compounds that present higher vapor concentrations were octanal ( $0.067 \pm 0.002$   $\text{g}\cdot\text{m}^{-3}$ ), linalool ( $0.027 \pm 0.001$   $\text{g}\cdot\text{m}^{-3}$ ), and citronellal ( $0.017 \pm 0.001$   $\text{g}\cdot\text{m}^{-3}$ ), which is probably a consequence of their content in the liquid mixture and their higher vapor pressures values (when compared to other oxygenated compounds) (Table 1). Nonanal, undecanal, neral, and dodecanal were quantified with percentages lower than 0.1 (%w/w), being considered traces (*t*) in the liquid phase (Table 1). However, the vapor concentrations of nonanal and neral were possible to be quantified, being higher than  $0.001$   $\text{g}\cdot\text{m}^{-3}$ , which is the lower value granted by the HS-GC analysis. The aldehydes undecanal and dodecanal were not identified in the vapor phase, due their low liquid composition and vapor pressure values (Table 1).

### II.3.2.2. Phases from the liquid–liquid equilibrium

The vapor concentrations of each component are presented in Table 3, for both solvents. In this table it is possible to observe that, in general, the increment of solvent in the systems (EO/S from 4/1 to 1/2) and the increase of water in the solvent [from 30 to 40 (%w/w)] induced higher concentrations of terpenes and oxygenated compounds in the vapor phases. This is probably due to the enhanced polarity of the mixtures [32], leading to the migration of the non-polar components such as terpenes [20] to the vapor phase. In the case of the oxygenated compounds, although they present a polar group (alcohol or aldehyde) and low vapor pressure values, when compared to the terpenes (Table 1), they also contain a non-polar carbon chain, contributing to their migration to the vapor phase. Contrasting to the crude EO, several components were not identified in the headspace of the LLE phases, mainly in the extract phases, probably due to their low mass fractions in the liquid mixtures (Table 2), while more components were quantified using EO/S = 1/1. Furthermore, since water is an odorless component, its vapor concentration was not determined.

**Table 3** – Experimental vapor concentrations ( $C_i^v$ , in  $\text{g}\cdot\text{m}^{-3}$ ) and estimated odor intensities ( $\Psi_i$ ) for each component in raffinate and extract phases, at the temperature  $T = 298.2$  K and pressure  $p = 1.02 \times 10^5$  Pa<sup>a</sup>, using different essential oil to solvent mass ratios (EO/S), for both solvents.

Solvent 30 (%w/w) water		Raffinate Phases			$\Psi_i$		
Component ( <i>i</i> )	$C_i^v$ ( $\text{g}\cdot\text{m}^{-3}$ ) <sup>b</sup>			$\Psi_i$			
	EO/S = 4/1	EO/S = 1/1	EO/S = 1/2	EO/S = 4/1	EO/S = 1/1	EO/S = 1/2	
Ethanol	38 ± 1	130 ± 7	121 ± 5	55 ± 2	113 ± 6	109 ± 4	
<i>Terpenes</i>	10.7 ± 0.1	27.1 ± 0.7	27.1 ± 0.9	80 ± 1	126 ± 3	126 ± 4	
$\alpha$ -Pinene	0.59 ± 0.01	1.84 ± 0.05	1.86 ± 0.04	42.0 ± 0.8	73 ± 2	74 ± 1	
Limonene	10.08 ± 0.09	25.3 ± 0.7	25.3 ± 0.8	37.5 ± 0.3	53 ± 1	53 ± 2	
<i>Oxygenated</i>	0.030 ± 0.006	0.071 ± 0.003	0.049 ± 0.005	23 ± 5	38 ± 2	28 ± 3	
Octanal	0.023 ± 0.002	0.047 ± 0.001	0.037 ± 0.001	11 ± 1	14.4 ± 0.3	13.3 ± 0.4	
Octanol		0.001 ± 0.001			1.9 ± 0.2		
Nonanal	0.002 ± 0.001	0.006 ± 0.001	0.005 ± 0.001	3 ± 1	4.8 ± 0.5	4.4 ± 0.2	
Citronellal	0.002 ± 0.001	0.008 ± 0.001	0.005 ± 0.001	5 ± 2	7.4 ± 0.8	6.4 ± 0.5	
Linalool	0.005 ± 0.001	0.009 ± 0.001	0.005 ± 0.001	7 ± 1	9.0 ± 0.8	7.5 ± 0.4	
Solvent 30 (%w/w) water		Extract Phases			$\Psi_i$		
Component ( <i>i</i> )	$C_i^v$ ( $\text{g}\cdot\text{m}^{-3}$ ) <sup>b</sup>			$\Psi_i$			
	EO/S = 4/1	EO/S = 1/1	EO/S = 1/2	EO/S = 4/1	EO/S = 1/1	EO/S = 1/2	
Ethanol	34 ± 1	154 ± 1	147 ± 3	52 ± 2	125 ± 1	122 ± 2	
<i>Terpenes</i>	9.5 ± 0.4	34 ± 2	34.9 ± 0.7	76 ± 3	133 ± 9	134 ± 3	
$\alpha$ -Pinene	0.55 ± 0.03	1.9 ± 0.2	2.0 ± 0.1	40 ± 2	75 ± 5	76 ± 2	
Limonene	9.0 ± 0.4	33 ± 2	32.9 ± 0.6	36 ± 1	58 ± 4	58 ± 1	
<i>Oxygenated</i>	0.018 ± 0.002	0.06 ± 0.01	0.074 ± 0.004	16 ± 1	22 ± 3	29 ± 2	
Octanal	0.015 ± 0.002	0.051 ± 0.008	0.059 ± 0.003	10 ± 1	15 ± 2	15.5 ± 0.8	
Citronellal		0.007 ± 0.001	0.009 ± 0.002		7.3 ± 0.9	8 ± 2	
Linalool	0.003 ± 0.001	0.006 ± 0.002	0.007 ± 0.002	6 ± 2	8 ± 3	8 ± 2	
Solvent 40 (%w/w) water		Raffinate Phases			$\Psi_i$		
Component ( <i>i</i> )	$C_i^v$ ( $\text{g}\cdot\text{m}^{-3}$ ) <sup>b</sup>			$\Psi_i$			
	EO/S = 4/1	EO/S = 1/1	EO/S = 1/2	EO/S = 4/1	EO/S = 1/1	EO/S = 1/2	
Ethanol	36 ± 2	117 ± 1	114 ± 3	54 ± 4	106 ± 1	105 ± 3	
<i>Terpenes</i>	10.4 ± 0.6	25 ± 1	27.0 ± 0.9	79 ± 4	123 ± 7	126 ± 4	
$\alpha$ -Pinene	0.57 ± 0.04	1.8 ± 0.1	1.9 ± 0.1	41 ± 3	72 ± 4	74 ± 2	
Limonene	9.9 ± 0.5	23 ± 1	25.1 ± 0.9	37 ± 2	51 ± 3	53 ± 2	
<i>Oxygenated</i>	0.035 ± 0.003	0.091 ± 0.004	0.076 ± 0.002	28 ± 2	45 ± 2	40 ± 1	
Octanal	0.023 ± 0.001	0.056 ± 0.004	0.049 ± 0.002	11.4 ± 0.4	15 ± 1	14.6 ± 0.5	
Octanol		0.002 ± 0.001	0.001 ± 0.001		2.2 ± 0.1	1.8 ± 0.2	
Nonanal	0.002 ± 0.001	0.007 ± 0.001	0.006 ± 0.001	3.4 ± 0.9	5.13 ± 0.08	4.9 ± 0.3	
Neral		0.002 ± 0.001	0.002 ± 0.001		3.3 ± 0.4	3.4 ± 0.3	
Citronellal	0.003 ± 0.001	0.011 ± 0.001	0.008 ± 0.001	6 ± 1	8 ± 1	8 ± 1	
Linalool	0.006 ± 0.001	0.014 ± 0.001	0.010 ± 0.001	8 ± 1	10.4 ± 0.3	9.3 ± 0.2	
$\alpha$ -Terpineol		0.001 ± 0.001			1.66 ± 0.04		
Solvent 40 (%w/w) water		Extract Phases			$\Psi_i$		
Component ( <i>i</i> )	$C_i^v$ ( $\text{g}\cdot\text{m}^{-3}$ ) <sup>b</sup>			$\Psi_i$			
	EO/S = 4/1	EO/S = 1/1	EO/S = 1/2	EO/S = 4/1	EO/S = 1/1	EO/S = 1/2	
Ethanol	31 ± 2	143 ± 2	147 ± 5	50 ± 4	120 ± 2	122 ± 5	
<i>Terpenes</i>	8.1 ± 0.9	34 ± 1	35 ± 1	71 ± 8	132 ± 5	134 ± 6	
$\alpha$ -Pinene	0.47 ± 0.05	1.91 ± 0.07	2.0 ± 0.1	37 ± 4	75 ± 3	76 ± 3	
Limonene	7.7 ± 0.9	32 ± 1	33 ± 1	34 ± 4	57 ± 2	58 ± 2	
<i>Oxygenated</i>	0.022 ± 0.006	0.081 ± 0.008	0.070 ± 0.003	17 ± 5	33 ± 3	27 ± 1	
Octanal	0.015 ± 0.002	0.062 ± 0.007	0.059 ± 0.004	10 ± 1	16 ± 2	15 ± 1	
Nonanal	0.006 ± 0.001			4.9 ± 0.6			
Citronellal		0.010 ± 0.002	0.010 ± 0.001		8 ± 1	8 ± 1	
Linalool	0.004 ± 0.001	0.009 ± 0.001	0.006 ± 0.001	7 ± 1	9 ± 1	7.6 ± 0.5	

<sup>a</sup> Standard uncertainties  $u$  are  $u(T) = 0.1$  K,  $u(p) = 1 \times 10^3$  Pa,  $u(C_i^v)$  presented after the vapor concentration, and  $u(\Psi_i)$  after the odor intensity value.

<sup>b</sup> Vapor concentrations above the liquid phases from Table 2.

### II.3.3. Aroma profile

#### II.3.3.1. Crude orange essential oil

According to the experimental  $\Psi_i$  values (Table 1),  $\alpha$ -pinene dominated the odor of crude EO, in spite of its low vapor concentration when compared with limonene ( $1.43 \pm 0.04$  and  $19.4 \pm 0.7 \text{ g}\cdot\text{m}^{-3}$ , respectively). This may be explained by the low *ODT* value of  $\alpha$ -pinene ( $2.88 \times 10^{-4} \text{ g}\cdot\text{m}^{-3}$ ), together with its high power law exponent (0.49). As it can be confirmed in Table 1, the  $\Psi_i$  followed the order:  $\alpha$ -pinene ( $65 \pm 2$ ) > limonene ( $48 \pm 2$ ) > octanal ( $16.1 \pm 0.5$ ) > linalool ( $13.1 \pm 0.5$ ) > citronellal ( $9.80 \pm 0.06$ ) > nonanal ( $5.6 \pm 0.1$ ). Although octanol, neral,  $\alpha$ -terpineol, and geranial were quantified in the vapor phase, their  $\Psi_i$  values are minor when compared to the other components, denoting a low contribution to the EO aroma.

The aroma of citrus EOs has been attributed to oxygenated compounds [1,11,14]. In fact, the  $\Psi$  of the oxygenated compounds ( $58 \pm 2$ ), even with low mass percentages in the liquid mixture, is higher than limonene ( $48 \pm 2$ ), which represents more than 96 (%*w/w*). This is mainly a consequence of the low *ODT* values of the oxygenated compounds (Table 1).

#### II.3.3.2. Phases from the liquid–liquid equilibrium

The estimated  $\Psi_i$  of the raffinate and extract phases are shown in Table 3. Albeit the similarity of both phases in terms of the contribution of each component on the odor of the mixture, in general, when EO/S = 1/1 and 1/2 were used, the  $\Psi_i$  in the extract phases were slightly higher than those of raffinate phases, mainly for the monoterpenes (limonene and  $\alpha$ -pinene). As already noted, analyzing Table 3, the  $C_i^v$  of these components were higher in the extract phase than in the raffinate (for EO/S = 1/1 and 1/2), no matter the water content in the solvent. Limonene and  $\alpha$ -pinene are non-polar molecules (hydrocarbons [20]) and, because of this, when in a polar mixture (extract phases) they will be ‘pushed up’ from the mixture (higher concentration of molecules in the headspace) [32]. Differently, oxygenated compounds, which possess a polar group in their molecular structure, tend to be more retained in the liquid phase [32]. It was observed that the components with higher contribution to the aroma of the LLE phases were ethanol ( $\Psi = 52 - 125$ ) >  $\alpha$ -pinene ( $\Psi = 37 - 76$ ) > limonene ( $\Psi = 34 - 58$ ) > octanal ( $\Psi = 10 - 16$ ) > linalool ( $\Psi = 6 - 10$ ) > citronellal ( $\Psi = 5 - 8$ ) > nonanal ( $\Psi = 3 - 5$ ) > octanol ( $\Psi = 2$ ). This tendency was also observed in the crude EO (Table 1) (except for ethanol, which is not present in the crude EO). In spite of the divergences found in the liquid compositions among the crude EO and the LLE phases, the concentrations in the headspace

were similar and, consequently, their odor intensities were close, and both raffinate and extract phases exhibited similar aroma profiles. The effect of the EO/S ratio and water content in the solvent are discussed next.

### **II.3.3.3. Effect of essential oil/solvent ratio**

Gonçalves et al. [5] studied the fractionation of limonene and linalool mixtures in a perforated rotating disc contactor (PRDC) using hydroalcoholic solvents with the same composition as used in this study [ethanol 30 and 40 (%w/w) water]. The authors observed that the increase in the solvent/ feed ratio (S/F) led to greater extraction of limonene and linalool, and lesser migration of solvent from the extract to the raffinate phase. This behavior may be also verified in the liquid composition of the LLE phases in Table 2. The authors also observed that the increase in S/F caused a decrease in linalool content in the extract phase compared to limonene (lower linalool content in the extract phase on a solvent-free basis, %LE) [5].

Analyzing the effect of the EO/S ratio on the  $\Psi_i$  of the phases, it may be confirmed in Table 3 that the increasing on the amount of solvent in the system, from 4/1 to 1/1 enhanced the  $\Psi_i$  in both the raffinate and solvent phases, independent of the solvent used. Therefore, the odor of limonene and  $\alpha$ -pinene will be more intense in the phases than in the typical orange EO, which means more citrus, herbaceous, and woody (see the classification of the components into the olfactory families in Table 1). Moreover, the increase in solvent in the system enabled the identification of some oxygenated compounds in the headspace, for example, citronellal in the extract phase [EO/S = 1/1 and 1/2, solvent 30 (%w/w) water], and octanol and neral in the raffinate phase [EO/S = 1/1 and 1/2, solvent 40 (%w/w) water] (Table 3). However, in general, no relevant differences were observed in terms of vapor concentrations as well as odor intensity between the phases using EO/S = 1/1 and 1/2, for both solvents. Therefore, EO/S = 1/1 can be highlighted as the best ratio to be applied industrially, since less solvent is required.

### **II.3.3.4. Effect of water content in the solvent**

In Table 3 it is possible to observe that the increase in water in the solvent caused no relevant changes in  $\Psi_i$ . Nevertheless, discounting the presence of ethanol, the odor profiles of both phases were similar to those obtained for crude EO, in terms of components with higher  $\Psi_i$ . As the increase of water in the solvent did not strongly influence the  $\Psi_i$ , the solvent 40 (%w/w) water is the most advantageous to this fractionation procedure, considering solvent cost (the least expensive due to the minor concentration of ethanol).

## II.3.4. Classification into olfactory families

### II.3.4.1. Crude orange essential oil

The PR methodology was applied to the classification of the perceived odor into olfactory families, elicited from the studied mixtures. The PR constructed for crude EO (Fig. 1a) revealed citrus (37%) as the primary olfactory family with herbaceous (27%), woody (13%), floral (13%), green (7%), and fruity (3%) *nuances* (subtle distinction from the main olfactory family). Citrus scent was mainly influenced by the existence of limonene in its liquid composition and vapor concentration (Table 1). The orange EO aroma is in accordance with previous classifications [37,39–41]. Teixeira et al. [26] classified an orange EO (the species was not specified by the authors) using the PR predictive methodology from the liquid composition. These authors described citrus (44%) as the predominant olfactory family, with woody and fruity scents and light floral and green *nuances*. Comparing the experimental PR constructed in this study and the predicted PR of Teixeira et al. [26], the main difference found was the absence of the herbaceous scent, which is the primary olfactory family of  $\alpha$ -pinene. This is because  $\alpha$ -pinene was not identified in the orange EO studied by Teixeira et al. [26]. In addition, the differences found may be due to the orange variety or to the method used for EO extraction and analysis, leading to distinct EO compositions.

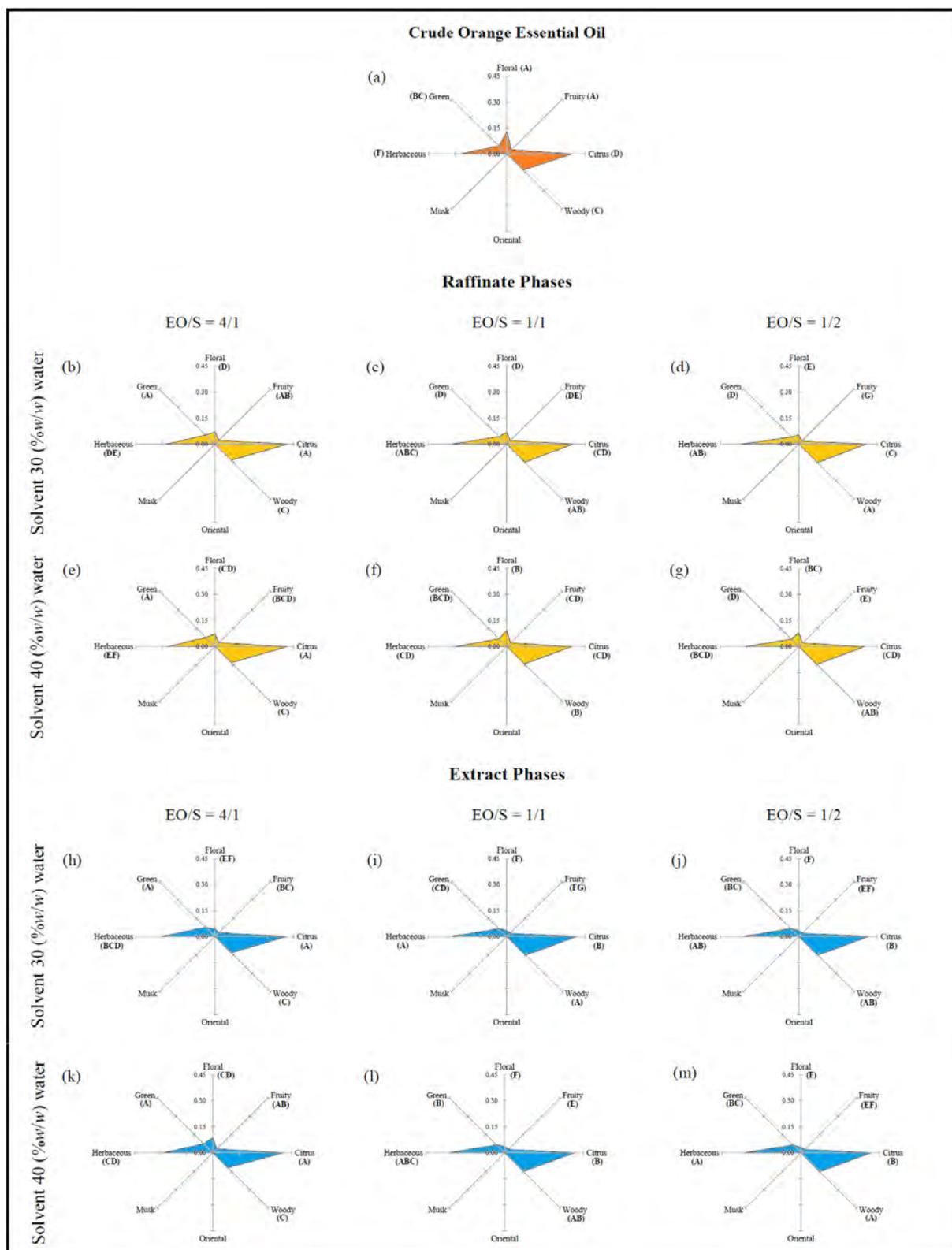


Fig. 1 - Perfumery Radars: (a) crude orange essential oil; LLE phases: (b) to (g), raffinate phases; (h) to (m), extract phases. Water in the solvent: (b) to (d) and (h) to (j), 30 (% w/w); (e) to (g), and (k) to (m), 40 (% w/w). Essential oil to solvent mass ratio (EO/S): (b), (e), (h), and (k), 4/1; (c), (f), (i), and (l), 1/1; (d), (g), (j), and (m), 1/2. Olfactory families followed by the same letter do not show significant differences by Duncan's test ( $P \leq 0.05$ ).

### II.3.4.2. Phases from the liquid–liquid equilibrium

As observed for the crude orange EO (Fig. 1a), the aroma of raffinate and extract phases was dominated by the citrus scent (37 – 42%, Fig. 1b–1m). Apparently, the EO/S ratio and water content in the solvent did not affect strongly the PRs of both phases. However, statistically, we can point out that the aroma of the phases was less floral than the crude EO, since lower amount of oxygenated compounds was quantified in the headspace (Table 3). The extract phases using EO/S = 1/1 and 1/2 (Fig. 1h–1m) were less floral than the raffinate (Fig. 1b–1g) and crude EO (Fig. 1a), but they were a little more citrus, herbaceous, and woody, since the  $C_i^v$  of the terpenes was increased in the extract phases. In spite of the differences in the liquid composition of the LLE phases and enhanced  $\Psi$  of limonene and  $\alpha$ -pinene with the increase of solvent (EO/S from 4/1 to 1/1) (Table 3), overall, the aroma profiles of the raffinate and extract phases were close to crude orange EO, what concerns to the main olfactory families, citrus and herbaceous. This finding can be explained by the PR methodology, which consists of a normalization among olfactory families identified in the mixtures to verify the dominant scent in the mixture. This approach enables the comparison of PRs in a scale independent of  $\Psi$  values [26].

The results found in this study can be compared to prior work [10], where the crude acid lime EO was submitted to the fractionation process using different ethanol/ water mixtures. In general, the aroma profile of the LLE phases was equivalent to the typical acid lime EO aroma, independently of the solvent, but with less floral scent, as well as discussed for the orange EO. As already mentioned, the loss of floral scent is mainly related to the low concentration of oxygenated compounds in the vapor phases.

### II.3.5. Sensory analysis

A model mixture of crude EO was prepared as described in section 2.6 and analyzed by the panel. According to the results, this mixture was dominated by a strong citrus odor, as observed for crude EO. No relevant variations in the aroma of crude EO and its model mixture were detected by the panel. Therefore, it is possible to infer that the components identified in the headspace ( $\alpha$ -pinene, limonene, octanal, linalool, citronellal, and nonanal) are, in fact, the main responsible for the typical orange aroma. In relation to the LLE phases, their aromas were also dominated by a citrus character. In almost all the phases, herbaceous scent was identified as the second dominant odor. Floral and green *nuances* were also identified in the phases, but they were less evident. Thus, the two dominant olfactory families evaluated by the PR methodology,

citrus and herbaceous (Fig. 1a) matched with those identified in the sensory analysis, emphasizing that the PR is an efficient tool to describe the aroma of a liquid mixture.

When asked about the most pleasant aroma between the phases, the majority of the panelists selected the extract phase as more agreeable, and described it as soft, with fresh orange odor, less acidic, and with more floral scent. In relation to the raffinate phases, panelists described them as herbaceous and more acidic than the extract phases, resembling the odor of mature orange. This may be due to the high concentration of limonene in this phase, as well as to the possible degradation associated to the instability of this component when exposed to the light and air [9] during sensory analysis. About the fresh feeling of the extract phases, it is probably related to the high concentration of ethanol. Interestingly, albeit the high  $\Psi$  values for ethanol (Table 3), panelists did not identify alcoholic odor in any of the samples. This behavior can be explained based on previous assays using ethanol as solvent of fragrance mixtures [42]. The authors applied the Perfumery Ternary Diagram<sup>®</sup> methodology for the prediction and mapping of the odor character of ternary to quaternary fragrance mixtures. Some systems composed of top (limonene), middle (geraniol) and base (vanillin) notes, diluted in different amounts of ethanol (solvent) were studied. The results showed that using 30 and 50 (%*x/x*) of ethanol in the composition of the liquid mixture (which corresponds to the mass percentages of ethanol present in the extract phases), limonene (top note) was strongly perceived. Therefore, comparing the data obtained with those reported by these authors, it may be inferred that the same behavior may be observed in the case of extract phases, in which ethanol was not identified by the panelists even at high concentrations, with limonene as the dominant odor.

The preference of the panelists, as final consumers, for the extract phase as the most pleasant one is an interesting information since, technically, these phases are desirable for application in beverages, being highly soluble in aqueous solutions [43]. Moreover, the presence of ethanol enables degradation reactions to be reduced [44] and intensified the terpenes odor. Finally, based on this study, we can highlight that the extract phase using EO/S = 1/1 and ethanol 40 (%*w/w*) water was the best candidate in terms of sensory quality to be incorporated in liquid products, such as beverages and perfumes.

## II.4. Conclusions

Concerning to the liquid mixtures, chemical analysis revealed monoterpenes as the major group of components present in the crude orange EO and raffinate phases, whereas the extract phases were abundant in solvent (ethanol and water). In terms of odor intensity, results indicated that  $\alpha$ -pinene and limonene dominated the aroma of the crude EO and that ethanol,  $\alpha$ -pinene, and limonene dominated the odor of the LLE phases. The raffinate and extract phases exhibited an aroma profile similar to that of the crude EO, compared to the components that have a greater contribution to the final aroma of the mixtures. Therefore, the headspace analysis highlighted  $\alpha$ -pinene > limonene > octanal > linalool > citronellal > nonanal as the components most responsible for the typical orange EO aroma, which was also confirmed by the sensory analysis using a model orange EO mixture.

The increase in solvent in the systems from EO/S = 4/1 to 1/1 intensified limonene and  $\alpha$ -pinene odors. Conversely, the increase of water content in the solvent did not lead to any relevant effect on the odor intensities of all components. From the PR, the crude EO was classified as citrus and herbaceous scent, with woody, floral, green, and fruity *nuances*. The sensory analysis supported the same tendency. The LLE phases presented the same classification, and almost no apparent differences were observed among the mixtures, except the fact that the extract phases were less floral, but more citrus, herbaceous, and woody than the crude EO (for EO/S = 1/1 or 1/2). Moreover, all mixtures were identified as ‘typical orange odor’ by the panelists, and the ethanol odor was not perceived by them, being possibly associated with a “fresh” feeling.

Based on the present study it is possible to infer that the solvent extraction technique using ethanol/water mixtures applied to the fractionation of crude orange EO led to extract phases with typical orange EO. Furthermore, the majority of the panelists demonstrated preference for the extract phase, in terms of aroma qualities. Finally, this study highlights that the extract phase using EO/S = 1/1 and ethanol with 40 (%w/w) water was the best candidate in terms of sensory quality and lesser use of solvent to be incorporated in liquid products, such as perfumes and beverages.

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## CHAPTER III: Fractionation of citrus essential oil by liquid–liquid extraction using a perforated rotating disc contactor

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### Fractionation of citrus essential oil by liquid–liquid extraction using a perforated rotating disc contactor



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#### ABSTRACT

Citrus essential oils are important raw materials used in the formulation of many products, including soft and alcoholic drinks, flavoring agents, cosmetics, perfumes and toiletries. With the aim of improving the quality and, consequently, the price of the product, the separation of terpenic hydrocarbons and oxygenated compounds is required. The fractionation of essential oils may be achieved using diverse techniques, including liquid–liquid extraction using the appropriate solvents. This study was aimed at the fractionation of citrus essential oil model systems, composed of limonene and linalool mixtures, and crude orange essential oil (COEO) using continuous equipment known as a perforated rotating disc contactor (PRDC), in which mixtures of ethanol and water were used as the solvent. The effect of some variables, including disc rotation speed (DRS), linalool content in the feed (%LF), water content in the solvent ( $w_{A,S}$ ) and the ratio between the solvent and the feed mass flows (S/F), on process performance, using model mixtures, was studied. The fractionation process using the PRDC achieved concentration of linalool in the extract, on a solvent-free basis, 7-fold using a hydroalcoholic solvent with a water content of 30% by mass, and close to 10-fold using a solvent with 40% water by mass. With respect to the fractionation of COEO, the extraction indices reported here were in accordance with those determined for model systems, being obtained a concentration of oxygenated compounds of 10-fold using solvent with 30% of water and 15-fold using solvent with 40% of water.

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### III. Highlights

- Fractionation of citrus essential oil.
- Liquid–liquid extraction process using a PRDC and hydroalcoholic solvents.
- Mass transfer coefficients and the number of transfer units were evaluated.
- The concentration of oxygenated compounds in the extract phase was observed.

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### III.1. Introduction

Essential oils, as raw materials, are an important commodity on the world market. In the last year, essential oil exportation amounted to almost  $221 \cdot 10^3$  tons, corresponding to about US\$ 4 billion in trade value. Nowadays, Brazil is the main essential oil producer, with close to 25% of world's exports (almost  $65 \cdot 10^3$  tons). This fact is due to the wide production of citrus essential oil; Brazil is the top exporter of orange essential oil in the world (about 47% of exports) [1].

Essential oils are important constituents for the formulation of food and chemical products, mainly citrus essential oils, such as orange, lemon and lime. They are used in the preparation of soft and alcoholic drinks, flavoring and additive agents, and in the composition of perfumes, cosmetics, toiletries and others products [2–5].

Citrus essential oils are characterized as mixtures of several components, such as terpenes, sesquiterpenes, aldehydes, alcohols and esters, but can be simplified as a mixture of terpene hydrocarbons, oxygenated compounds and non-volatile residues, such as pigments and waxes [3,6,7]. The oxygenated compounds are, generally, those mainly responsible for the characteristic flavor of citrus essential oils and, unlike the hydrocarbon terpenes, present greater stability. Thus, the removal of hydrocarbons is an important step to provide better quality and stability of the product, thereby reducing the development of off-flavors [3,6–10]

In relation to trade value, the ranking of the main essential exporters is as follows: India, China, the United States of America, France, the United Kingdom and Brazil. Moreover, in the perfume, cosmetics and toiletries market, the ranking of the main exporters by trade value is: France, the United States of America, Germany, Ireland and Italy, with Brazil in the 21th position [1]. The trade value is usually related to the quality of the essential oil and its source (e.g. citrus fruit, eucalyptus leaves and flower petals). Thus, with the aim of improving the commercial value of essential oils, and to achieve better integration in the cosmetics market, fractionation processes are required.

Nowadays, the usual industrial fractionation of citrus essential oil is by vacuum distillation, which can present some problems once the boiling points of the oxygenated compounds are generally close to the boiling points of the terpenes [2]. Moreover, this technique generally requires a complex vacuum control and can present several problems related to the start up and stabilization of the process [11]. In this case, other alternative techniques of citrus essential oil fractionation are required.

Among the several methods applied to provide separation between terpenes and oxygenated compounds, a previous study [3] focused on the thermodynamic approach in which model citrus essential oils and crude orange essential oil were used. This study showed that fractionation is possible by the use of a liquid–liquid extraction technique (or solvent extraction), using ethanol and water mixtures as the solvent. Actually, the use of ethanol and water mixtures for the fractionation of essential oils has been studied [3,6,9,10,12,13]. In these studies, was possible to obtain fractions enriched in oxygenated compounds.

Studies based on the use of solvent extraction applied to the fractionation of essential oils consist, mostly, of the experimental determination and thermodynamic modeling of liquid–liquid equilibrium data. However, studies that present experimental data of essential oil fractionation using extraction equipment which can be used in industrial scale are rare or even non-existent.

The equipment used for liquid–liquid extraction may present several configurations and must promote contact between the liquids, create droplets of a dispersed phase in a continuous phase and provide a large area of contact between the phases to improve mass transfer. In addition, the apparatus must be able to establish the separation of the phases [14]. The perforated rotating disc contactor (PRDC) is a column with inner perforated rings, which provides good dispersion between the phases. In general, the PRDC is indicated for systems with low interfacial tension [15], and has been used by several authors to promote the fractionation of different systems [15–20]. The PRDC proved to be efficient in separation processes using liquid–liquid extraction, with a good mass transfer performance and controllability [20].

The aim of this study was to use the PRDC as a novel and alternative technology to promote the fractionation of citrus essential oils, using mixtures of ethanol and water as the solvent stream. As a primary study, citrus essential oil model systems, composed of limonene and linalool were used as the feed stream. The equipment was operated continuously and in a countercurrent configuration, and the studied process variables were: (i) the disc rotation speed (DRS), (ii) solvent and feed mass flow ratio (S/F) and (iii) water content in the solvent ( $w_{4,S}$ ), as the manipulated variables, and (iv) the linalool content in the feed (%LF), as the disturbance variable.

The effect of the variables was analyzed over the performance of the process through the calculation of extraction indices, estimation of the solute overall volumetric mass transfer coefficient and estimation of the number of mass transfer units. In addition, once physical

properties such as density ( $\rho$ ) and dynamic viscosity ( $\eta$ ) of the output streams have a direct influence over the separation of the phases and the stability of the process, these variables were also measured.

Finally, crude orange essential oil (COEO) was also submitted to the fractionation process in PRDC, using the same operation procedures of model systems. In these trials, the manipulated variables DRS and S/F were maintained at pre-set values, chosen based on results from model system experiments. The extraction indices obtained herein are in accordance with those determined for model systems, being possible to obtain a concentration of oxygenated compounds of 10-fold using solvent with 30% of water and 15-fold using solvent with 40% of water.

## **III.2. Experimental**

### **III.2.1. Material**

Alcoholic solvents composed of ethanol with nominal water mass percentages of 30% and 40% were prepared by diluting absolute ethanol with a purity exceeding 99.8 (mass percentage) (Merck, Darmstadt, Germany) with deionized water (Millipore, Milli-Q, Bedford, MA, USA). The levels of water in the solvents were chosen according to a previous study [3], in which a good separation between the phases was achieved and significant changes were observed in the values of solvent selectivity and the distribution coefficients for oxygenated compounds. In fact, these solvents containing these water contents have been previously studied in other essential oil systems, such as oregano [6], bergamot [7] and lemon [12] model mixtures and crude bergamot essential oil [10].

As previously reported [3], the citrus essential oil model systems were prepared by mixing limonene and linalool. According to Gonçalves et al. [3], citrus essential oils can be studied as a mixture of their two main components: limonene, as the terpene fraction, and linalool, as the oxygenated fraction. Linalool is difficult to separate from terpenes, therefore it is considered the key component of the oxygenated fraction [21].

The mass percentages of linalool (%LF) adopted were:  $5.06 \pm 0.01\%$ ,  $9.70 \pm 0.02\%$  and  $15.00 \pm 0.03\%$ , where %LF was calculated according to Eq. (1). Although the orange essential oil generally presented lower amounts of oxygenated compounds than the %LF values adopted, the main reason for using high %LF values was to verify the actual impact of the oxygenated compound content in the essential oil on performance of the fractionation process.

$$\%LF = \frac{w_{2,F}}{w_{1,F} + w_{2,F}} \times 100 \quad (1)$$

where  $w_{1,F}$  and  $w_{2,F}$  are the mass fractions of the limonene and linalool in the feed stream, respectively. The components of the model systems were assigned as 1, limonene; 2, linalool; 3, ethanol; and 4, water.

Crude orange essential oil (COEO) was industrially extracted by cold pressing from the orange peels of a mixture of two varieties of *Citrus sinensis*: ‘Pera Rio’ and ‘Valencia’. The crude essential oil was processed and kindly donated by Louis Dreyfus Commodities (Bebedouro, SP, Brazil). In this case, although essential oils contain hundreds of compounds, the composition of COEO was determined in terms of the components having mass percentages equal to or greater than 0.01. The components present in COEO were identified using a gas chromatograph coupled to a mass spectrometer, as previously described by Gonçalves et al. [3]. Based on this work, the compounds in COEO can be clustered into two fractions: the terpene fraction, in which limonene is the major compound and the oxygenated compound fraction, in which linalool is the major representative component. In our study, the components of the system were assigned as 1, terpenes; 2, oxygenated compounds; 3, ethanol; and 4, water.

The purities and retention times of the pure components, limonene, linalool and ethanol, and the composition of the crude orange essential oil (COEO) were analyzed by gas chromatography using a GC-FID (Shimadzu, model GC 2010 AF, Japan) with an automatic injector (Shimadzu, model AOC 20i, Japan). The experimental analysis was performed in a DB-FFAP (nitroterephthalic acid-modified polyethylene glycol) capillary column (Agilent, USA), 0.25  $\mu\text{m}$ , 30 m x 0.25 mm internal diameter; helium was the carrier gas at 1.13  $\text{mL} \cdot \text{min}^{-1}$  rate, the injection temperature was 523.2 K, the column temperature was 373.2 to 513.2 K with temperature control (8  $\text{K} \cdot \text{min}^{-1}$  rate), detection temperature was 553.2 K, and the injection volume was 1.0  $\mu\text{L}$  with a 1:50 split ratio. The samples were diluted in 1-propanol (Sigma-Aldrich, 99.9 %, EUA) with a 1:1 mass ratio before injection.

The CAS numbers, purities, provenance and experimental values of the physical properties of the components used in the experiments regarding model systems are shown in Table 1. The physical properties such as density, viscosity and surface tension were collected from previous study [3].

**Table 1:** Chemical names, CAS numbers, mass fraction purities, provenance of the materials and physical properties at the temperature  $T = 298.2$  K.<sup>a</sup>

Material	Chemical name	CAS registry number	Purity <sup>b</sup>	Molar mass / g·mol <sup>-1</sup>	Source	$\rho^c$ / kg·m <sup>-3</sup>	$\eta^d$ / mPa·s	$\sigma^e$ / mN·m <sup>-1</sup>
Limonene	1-methyl-4-prop-1-en-2-yl-cyclohexene	5989-27-5	0.988	136.23	Sigma-Aldrich, USA	841.35*	0.92*	27.6*
Linalool	(±)-3.7-Dimethyl-1.6-octadien-3-ol	78-70-6	0.992	154.25	Sigma-Aldrich, USA	857.38*	4.57*	25.4*
Ethanol	ethanol	64-17-5	0.998	46.07	Merck, Germany	785.18*	1.06*	21.6*
Water	water	7732-18-5	-	18.02	-	997.04*	0.87*	71.1*
Ethanol (30% water)	-	-	-	-	-	847.63	1.80	25.3
Ethanol (40% water)	-	-	-	-	-	886.87	2.18	26.7
Crude Orange Essential Oil	-	-	-	-	Louis Dreyfus Commodities, Brazil	841.08*	0.90*	24.8*

<sup>a</sup> Standard uncertainties  $u$  are  $u(T) = 0.1$  K,  $u(\rho) = 0.01$ ,  $u(\eta) \leq 0.03$  and  $u(\sigma) \leq 0.1$ .

<sup>b</sup> Experimentally determined by gas chromatography, given as mass fraction.

<sup>c</sup> Density.

<sup>d</sup> Dynamic viscosity.

<sup>e</sup> Surface tension.

\* Experimental data from Gonçalves et al. [3].

## III.2.2. Methods

### III.2.2.1. Experimental apparatus

The continuous equipment used in all experiments was a PRDC (Fig. 1) which consists of a glass-made column with three regions: extraction region (Fig. 1, n. 1), upper separation region (Fig. 1, n. 2) and bottom separation region (Fig. 1, n. 3). The construction details are described in Fig. 1.

Ten polypropylene perforated discs (Fig. 1, n. 4) were used with the following construction details: diameter = 2.65 cm, number of perforations = 33, perforation diameter = 0.25 cm, distance between discs = 1.31 cm, disc thickness = 0.15 cm, diameter of axis perforation = 0.35 cm, free flow area (total perforation area) = 1.62 cm<sup>2</sup> and non-perforated area = 3.80 cm<sup>2</sup>.

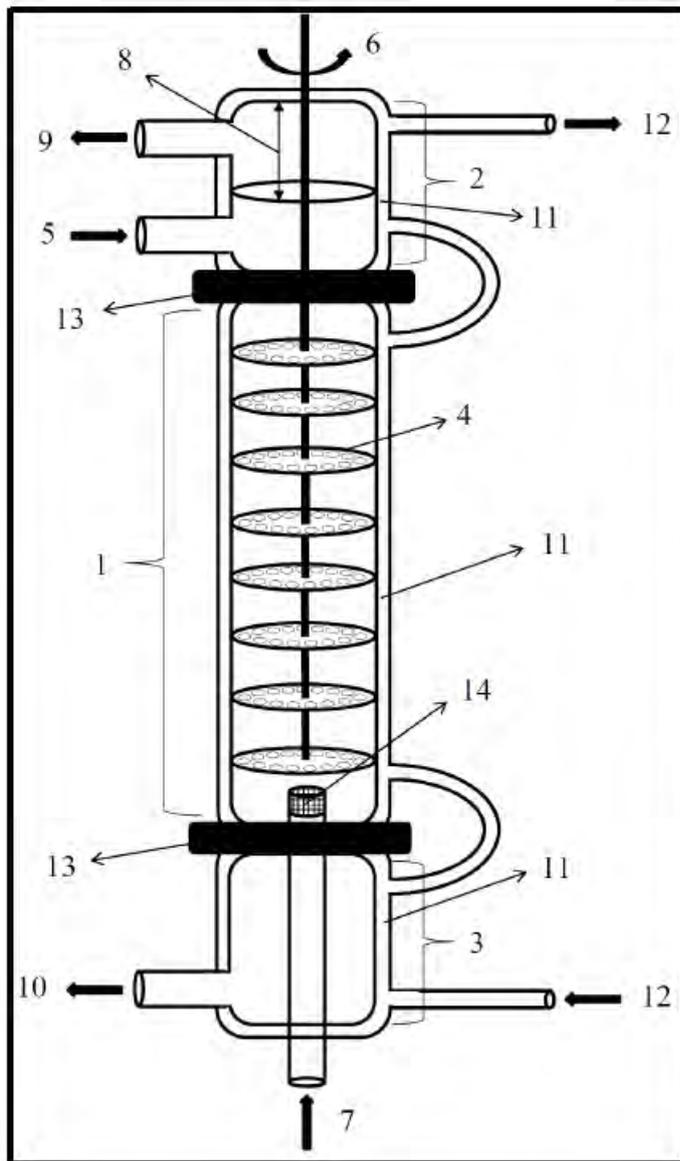
### III.2.2.2. Apparatus operation procedure

Citrus essential oil model mixtures with different linalool contents were previously prepared ( $5.06 \pm 0.01$ ,  $9.70 \pm 0.02$  and  $15.00 \pm 0.03\%$  of linalool, by mass) and subjected to a fractionation process using PRDC equipment, operating in a continuous and countercurrent manner. In the extraction experiments, the variables studied were: (i) the speed of disc rotation (150, 200 and 250 rpm), (ii) the solvent and feed mass flow ratio (0.5, 1.25, 2.0, 2.5; nominal values) and (iii) the solvent water content (ethanol with 30% and 40% water, by mass) as the manipulated variables, and (iv) the content of linalool in the feed stream (LF) ( $5.06 \pm 0.01$ ,  $9.70 \pm 0.02$  and  $15.00 \pm 0.03\%$ , by mass) as the disturbance variable.

For the fractionation of COEO, the values of all variables were set based on the results from experiments performed with model systems: disc rotation speed at 150 rpm; solvent and feed mass flow ratio at 1.25; and water contents in the solvent equal to 30 or 40%. It is important to highlight in this case, where crude oil was used, the content of oxygenated compounds in the feed stream is a pre-set value.

First, the column was filled with the solvent through the solvent inlet (Fig. 1 n. 5) and then the rotor responsible for the rotation of the discs (IKA, model Eurostar Power Control Visc P7, USA) was turned on (Fig. 1 n. 6), with a specific axis rotation speed. Then, the feed pump was turned on at  $2 \text{ mL}\cdot\text{min}^{-1}$  (from  $1.6$  to  $2.0 \text{ g}\cdot\text{min}^{-1}$ , depending on the feed density) and the equipment was fed with the model mixture through the feed inlet (Fig. 1 n. 7), initiating the fractionation process in the extraction region (Fig. 1 n. 1). The streams were introduced into the apparatus through digital peristaltic pumps (Cole Parmer Masterflex L/S model 77200-60,

USA) and the rotational speed of the disc was measured using a digital tachometer (Icel, model TC-5010, Brazil).



Upper separation region:

Height = 14.2 cm

External diameter = 5.0 cm

Internal diameter = 2.8 cm

Extraction region:

Height = 15.5 cm

External diameter = 5.0 cm

Internal diameter = 2.8 cm

Volume = 71.43 cm<sup>3</sup>

Bottom separation region:

Height = 10.6 cm

External diameter = 5.0 cm

Internal diameter = 2.8 cm;

Diameter of feed input = 1.6 cm

**Fig. 1** - Perforated Rotating Disc Contactor schematic illustration: (1) extraction region; (2) top separation region; (3) bottom separation region; (4) perforated disc; (5) solvent input; (6) disc axis; (7) feed input; (8) extract and raffinate streams interface height; (9) raffinate stream output; (10) extract stream output; (11) jacket; (12) water (at  $T = 293.15$  K) input and output; (13) screw to union the equipment parts; (14) feed stream distributor.

As the dispersed phase (raffinate) and continuous phase (extract) were mixed through the extraction region, raffinate accumulation occurred in the upper region (Fig. 1, no. 2). After approximately 10 minutes of continuous operation, the position of the interface was constant

(Fig. 1 n. 8), characterizing the stability of the process. At this point, the raffinate and extract phases were collected, and the input and output streams were pumped continuously, with no accumulation inside the apparatus.

The position of the interface between the raffinate and extract streams (Fig. 1, n. 8) was an important dependent variable, which was controlled during the entire process, since the stability of the process is directly related to the interfacial height.

The process performance was evaluated by the calculation of the indices described in sections 2.2.4.2, 2.2.4.3 and 2.2.4.4. Other variables, such as the raffinate and extract stream flows (Fig. 1 n. 9 and 10, respectively) were eventually manipulated through digital peristaltic pumps (Cole Parmer Masterflex L/S model 77200-60, USA) to keep the interfacial height constant.

All experiments were conducted under an atmospheric pressure of 749 mmHg and controlled temperature of  $298.2 \pm 0.1$  K using a thermostatic bath (Marconi, model MA-184, Brazil) that allowed water flow through the column jacket.

The input streams mass flows ( $\text{kg}\cdot\text{s}^{-1}$ ) were measured at the beginning and at the end of the process by weighing the mass (kg) pumped in 60 seconds. The output streams mass flows ( $\text{kg}\cdot\text{s}^{-1}$ ) were determined dividing the mass collected (kg) by the collection time for each sample (seconds).

Samples of the output streams (raffinate and extract streams) were collected at 15, 30, 45, 60, 75 and 105 minutes after the stabilization of the interface and were stored in amber glass bottles. After collection, the samples were immediately weighed and placed in disposable syringes. Each sample was diluted in 1-propanol (1:1 mass ratio) inside a gas chromatography vial to determine the composition as explained below.

### **III.2.2.3. Determination of sample composition**

The contents of limonene or terpenes, linalool or oxygenated compounds and ethanol in the feed and output streams were determined by GC-FID (Shimadzu, model GC 2010 AF with an automatic injector model AOC 20i, Japan) using the conditions described in the Material section. The external standard method was used for the quantification of the components.

The water content in the output streams (raffinate and extract), in the solvent inlet stream (ethanol and water mixtures) and in the pure components, i.e. ethanol, limonene, linalool and COEO, was determined by Karl Fischer titration (Metrohm, 787 KF Titrino, Switzerland) using Karl Fischer reagent (CombiTitrant 5 mg  $\text{H}_2\text{O}\cdot\text{mL}^{-1}$ , Merck, Darmstadt, Germany).

Samples from the last collection time of the output streams (105 minutes) were also subjected to the analysis of physical properties, such as density and dynamic viscosity. The experimental values of density and dynamic viscosity were measured according to previous studies [3,9]. The density measurements were performed in triplicate, with experimental standard deviations up to  $2.35 \text{ kg}\cdot\text{m}^{-3}$ . The standard deviations for dynamic viscosity measurements were less or equal to  $0.0394 \text{ mPa}\cdot\text{s}$ .

### III.2.2.4. Calculations

#### III.2.2.4.1. Mass balance

With the mass flow rates ( $\text{kg}\cdot\text{s}^{-1}$ ) and the composition of inlet (feed and solvent) and output streams (extract and raffinate), mass balance calculations were performed aiming to check the quality of the experimental results. The overall mass balance provides an overview of the process in relation to the inlet and output masses, not specifying the components, considering only the total mass flow of the streams. The error on the overall mass balance ( $E_{\text{OMB}}$ , in %) was determined as shown in Eq. (2). The relative error in the mass balance of a specific component  $i$  ( $E_{\text{MB}i}$ , in %) was calculated by Eq. (3).

$$E_{\text{OMB}} (\%) = \frac{|(F + S) - (E + R)|}{(F + S)} \times 100 \quad (2)$$

$$E_{\text{MB}i} (\%) = \frac{|(w_{i,F} \cdot F + w_{i,S} \cdot S) - (w_{i,E} \cdot E + w_{i,R} \cdot R)|}{(w_{i,F} \cdot F + w_{i,S} \cdot S)} \times 100 \quad (3)$$

where  $F$ ,  $S$ ,  $R$  and  $E$  are the feed, solvent, raffinate and extract streams mass flows, respectively, in  $\text{kg}\cdot\text{s}^{-1}$ .  $w_{i,F}$ ,  $w_{i,S}$ ,  $w_{i,R}$  and  $w_{i,E}$  are the mass fraction of the compound  $i$  in the feed, solvent, raffinate and extract streams, respectively.

#### III.2.2.4.2. Extraction indices

The total percentage of solute (linalool or oxygenated compounds) extracted from the feed ( $\% \text{EXT}_{\text{LOL}}$ ) and the composition of the solute in the extract phase on a solvent-free basis ( $\% \text{LE}$ , in %) were calculated. These indices are shown in Eq. (4) and (5) respectively, as proposed by Arce et al. [21] and Romero et al. [22].

$$\%EXT_{LOL} = \frac{w_{2,E} \cdot E}{w_{2,F} \cdot F} \times 100 \quad (4)$$

$$\%LE = \frac{w'_{2,E} \cdot E}{(w'_{2,E} \cdot E + w'_{1,E} \cdot E)} \times 100 \quad (5)$$

where the superscript ' corresponds to the composition on a solvent-free basis, calculated by Eq. (6).

$$w'_{2,E} = \frac{w_{2,E}}{(1 - w_{3,E} - w_{4,E})} \quad (6)$$

where  $w_{3,E}$  and  $w_{4,E}$  are the mass fractions of ethanol and water in the extract stream, respectively.

Other indices have been proposed in this study for better interpretation of the experimental data, such as the total percentage of the diluent (limonene or terpenes) extracted from the feed ( $\%EXT_{LIM}$ ) and the percentage of solvent migration to the raffinate stream ( $\%M_{SOLV}$ ), calculated according to Eq. (7) and (8), respectively.

$$\%EXT_{LIM} = \frac{w_{1,E} \cdot E}{w_{1,F} \cdot F} \times 100 \quad (7)$$

$$\%M_{SOLV} = \frac{w_{3,R} \cdot R + w_{4,R} \cdot R}{w_{3,S} \cdot S + w_{4,S} \cdot S} \times 100 \quad (8)$$

#### III.2.2.4.3. Evaluation of solute (linalool or oxygenated compounds) overall volumetric mass transfer coefficient

To evaluate the fractionation experiments, in relation to the mass transfer of the solute, the volumetric overall mass transfer coefficients ( $K_E \cdot a$ ) were calculated based on the concentration of the continuous phase (extract stream) in the extraction region of the PRDC (Fig. 1 n. 1).

According to a previous study [3], the partition coefficient of linalool, defined as the mass fraction of linalool that was transferred to the solvent-rich phase in relation to the mass fraction of linalool remaining in the oil-rich phase (at equilibrium condition), showed values lower than unity, independent of the water level in the solvent (values of the partition coefficient from 0.47 to 0.87 for the solvent with a water mass percentage of  $31.8 \pm 0.4$  and from 0.17 to 0.45 for the solvent with a water mass percentage of  $41.2 \pm 0.3$ ). When the linalool partition coefficients assumed values lower than unity for both solvents, a greater amount of linalool remained in the

terpene-rich phase in relation compared to that which migrated to the solvent-rich phase; this indicates that the solvent phase provides higher resistance to solute migration (linalool, in this case) [23].

The calculation of  $K_E \cdot a$  values, in  $\text{kg}_{\text{linalool}} \cdot \text{s}^{-1} \cdot \text{m}^{-3} \cdot [\text{kg}_{\text{linalool}} \cdot \text{kg}_{\text{extract}}^{-1}]^{-1}$  for model systems and  $\text{kg}_{\text{oxygen}} \cdot \text{s}^{-1} \cdot \text{m}^{-3} \cdot [\text{kg}_{\text{oxygen}} \cdot \text{kg}_{\text{extract}}^{-1}]^{-1}$  for systems with COEO, or  $K_E$  values in  $\text{m} \cdot \text{s}^{-1}$  if  $K_E$  is divided by the density of the extract phase, was evaluated according to the procedure proposed by Treybal [24] and used by several authors for different extraction column configurations, such as packed column [25], spray column [26,27] and PRDC [15–19,28] setups. In these studies, the principle that the solute is constantly transferred from the raffinate to the extract stream, i.e. the transference of the solute is not dependent on its concentration in the phases, was considered. Additionally, in these processes, the stream flows and the composition of the phases were considered on a solute-free basis. However, for the estimation proposed in this study, we considered that the transference of the solute (linalool or oxygenated compounds) from the raffinate phase to the extract phase is dependent on its concentration in these phases, which results in mass transfer that is not constant. Therefore, for the estimation of  $K_E \cdot a$  values (Eq. 9), the stream flows and the composition of the phases were considered on a total basis.

$$K_E \cdot a = \frac{E \cdot (w_{2,E} - w_{2,S})}{v \cdot \frac{\Delta w_A - \Delta w_B}{\ln\left(\frac{\Delta w_A}{\Delta w_B}\right)}} \quad (9)$$

where  $\Delta w_A$  is the absolute difference between  $w_{2,F}$  and  $w_{2,E}$ , and  $\Delta w_B$  is the absolute difference between  $w_{2,S}$  and  $w_{2,R}$  expressed as  $w_{2,E}^*$ ;  $v$  is the volume of the extraction region (Fig. 1 n.1) in  $\text{m}^3$ .

The term  $w_{2,S}$  corresponds to the mass fraction of linalool or oxygenated compounds in the solvent. As the solvent is composed only of ethanol and water, this value is zero. The term  $w_{2,E}^*$  is the mass fraction of linalool or oxygenated compounds in the extract stream at equilibrium with the raffinate stream.

The liquid–liquid equilibrium data determined by Gonçalves et al. [3] were used to adjust the parameters of polynomial models, from which the equations for the systems using solvents composed of ethanol with  $31.8 \pm 0.4$  and  $41.2 \pm 0.3$  water mass percentage were obtained (Eqs. 10 and 11, respectively).

$$w_{2,E}^* = -1.4722 \cdot w_{2,R}^2 + 0.7463 \cdot w_{2,R} \quad R^2 = 0.9983 \quad (10)$$

$$w_{2,E}^* = -1.0091 \cdot w_{2,R}^2 + 0.3929 \cdot w_{2,R} \quad R^2 = 0.9929 \quad (11)$$

By the use of the parameters presented in Eqs. 10 and 11, it was possible to calculate the composition of the extract stream, or the solvent-rich phase, under equilibrium conditions with the raffinate stream, or the terpene-rich phase.

#### III.2.2.4.4. Evaluation of the number of transfer units

Since the change in the composition with the height of the phases (raffinate and extract) as they pass through the PRDC is differential, the height of the column is not expressed in terms of stages or steps but in terms of transfer units [24]. Therefore, the estimation of the number of mass transfer units ( $N_{tOE}$ ), calculated for the transfer region of the PRDC (Fig. 1, n. 1) operating in a continuous and countercurrent configuration, was conducted according to Eq. (12), as suggested by Treybal [23,24].

$$N_{tOE} = \int_{w_{2,S}}^{w_{2,E}} \frac{dw_{2,E}}{w_{2,E} - w_{2,E}^*} + \frac{1}{2} \cdot \ln \frac{1 - w_{2,E}}{1 - w_{2,S}} + \frac{1}{2} \cdot \ln \frac{w_{2,E} \cdot \left( \frac{MM_1}{MM_2} - 1 \right) + 1}{w_{2,S} \cdot \left( \frac{MM_1}{MM_2} - 1 \right) + 1} \quad (12)$$

where MM is the molar mass of the compound, in  $\text{g} \cdot \text{mol}^{-1}$ .

The calculation of  $w_{2,Ei}^*$ , in each interval, was done according to Eq. (10) for the solvent composed of ethanol with 30% water by mass, and according to Eq. (11) for the solvent composed of ethanol with 40% water by mass.

This approach makes the differential column (PRDC) a multistage column. As in the calculation of  $K_E \cdot a$  (Eq. 9), for the use of Eq. (12), we considered that the transference of the solute to the extract phase is a function of its concentration in the streams. Therefore, the compositions of the streams were expressed on a total basis.

#### III.2.2.4.5. Statistical analysis

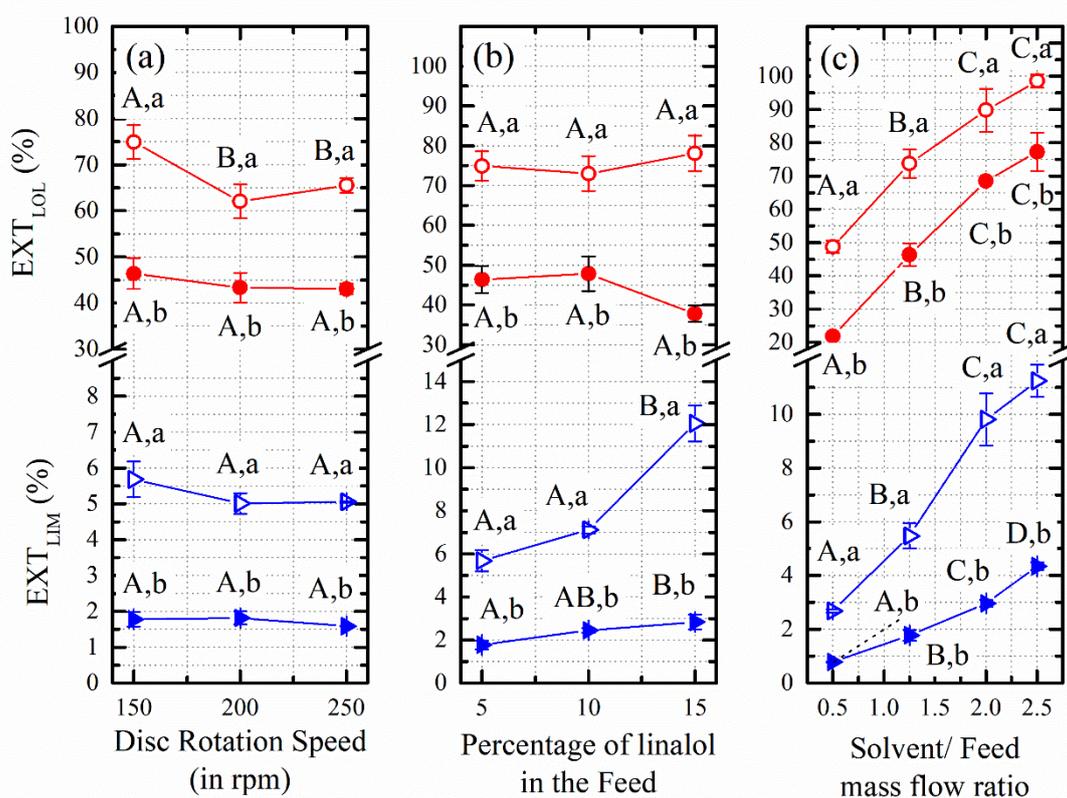
The experimental and calculated results were compared by variance analysis with Duncan's test at a significance level of  $P \leq 0.05$ , using SAS® software (version 9.2, SAS Institute Inc., Cary, NC, USA).

### III.3. Results and Discussion

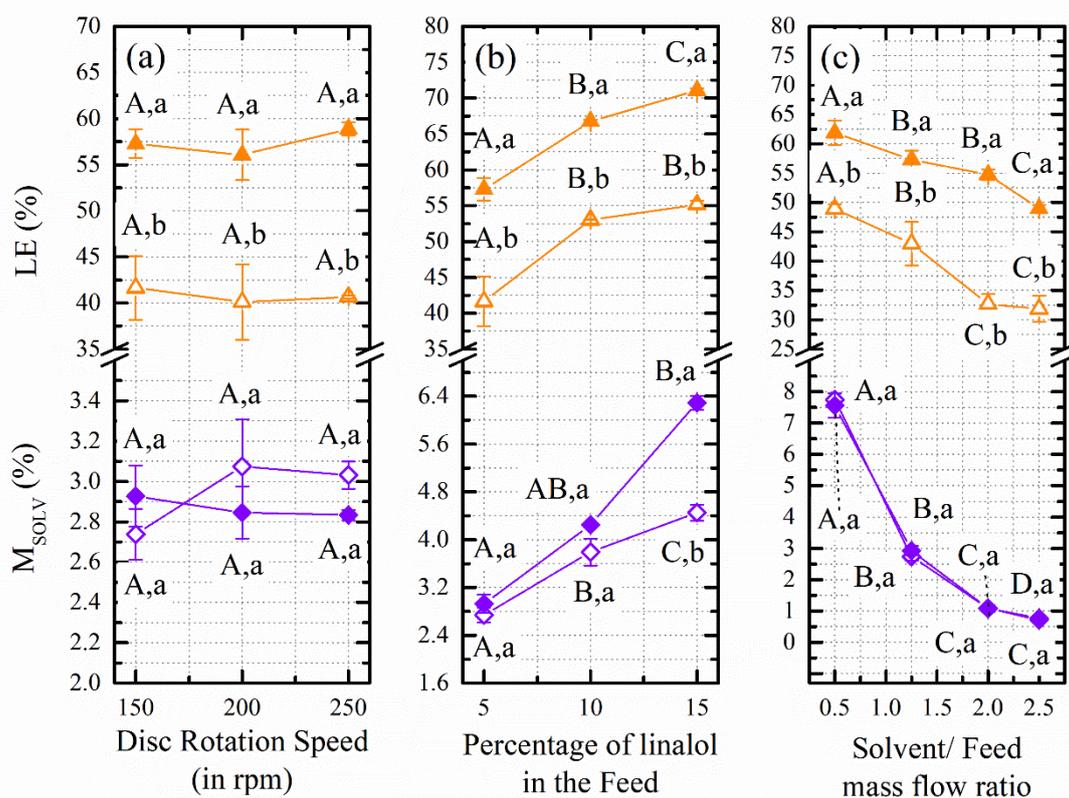
The error on the overall mass balance ( $E_{OMB}$ , Eq. 2) was not higher than 4.17% using ethanol with 30% water content and not higher than 3.58% using ethanol with 40% water content. With respect to the relative error in the mass balance of a specific component ( $E_{MBi}$ , Eq. 3), for all model systems, the values were up to 8.17% for limonene, 12.94% for linalool, 5.47% for ethanol and 9.79% for water. For the real systems, the highest errors were 3.54% for terpenes, 9.66% for oxygenated compounds, 5.49% for ethanol and 6.11% for water. The largest errors were related to the linalool component, or oxygenated compounds, since they were the minor components of the systems. However, in general, the  $E_{OMB}$  and  $E_{MBi}$  values were below 10%, which is suitable for continuous processes.

The  $\%EXT_{LOL}$  and  $\%EXT_{LIM}$  values, calculated according to Eq. (4) and (7), respectively, are shown in Fig. 2; the  $\%LE$  and  $\%M_{SOLV}$  values, calculated according to Eq. (5) and (8), respectively, are shown in Fig. 3; the values of  $K_E \cdot a$  and  $N_{IEO}$ , estimated according to Eq. (9) and (12), respectively, are shown in Fig. 4. The difference between the experimental values of the densities of the extract and raffinate streams, and the difference between the experimental values of the dynamic viscosities of the extract and raffinate streams ( $\Delta\rho$  and  $\Delta\eta$ , respectively), are shown in Fig. 5.

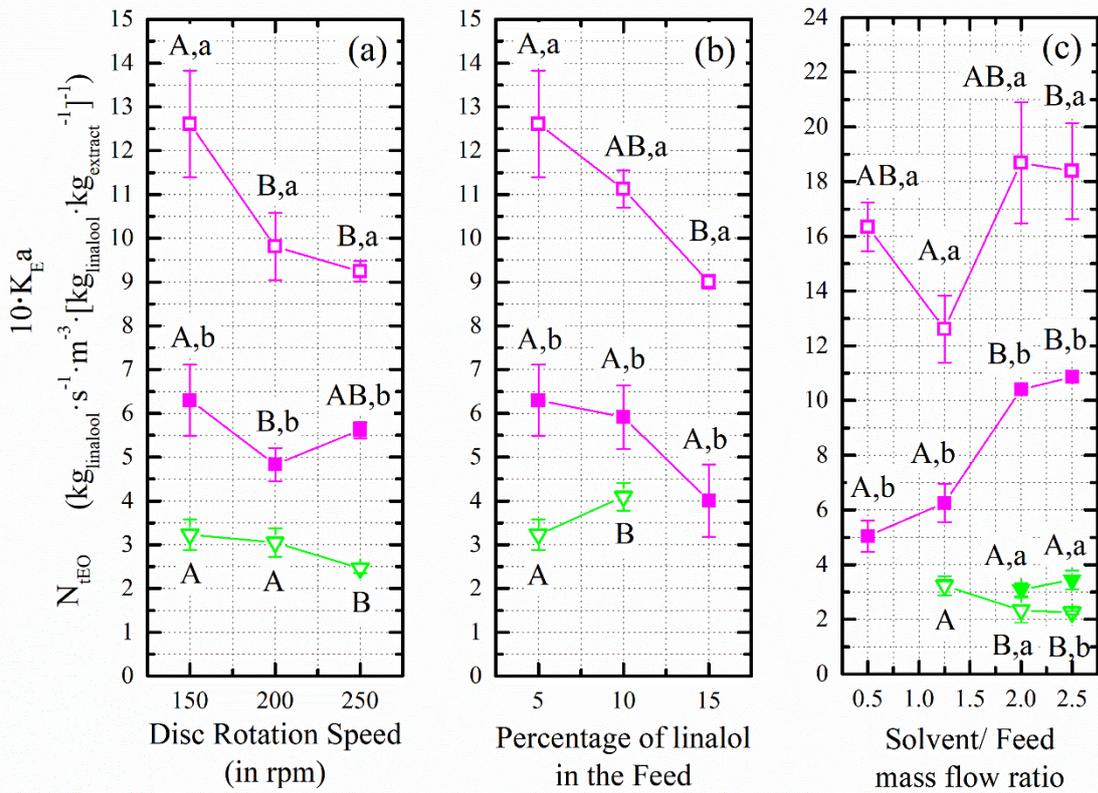
According to our previous study [3], for the ethanolic solvent with the higher water content (40% by mass) the limonene and linalool distribution coefficient values were smaller than those regarding the solvent with 30% water by mass, so the extraction indices decreased with an increase in the water content of the solvent. However, the selectivity of the solvent with 40% water by mass was higher than that regarding the solvent with 30% water by mass; therefore, the  $\%LE$  values increased with an increase in the water content of the solvent (Fig. 3).



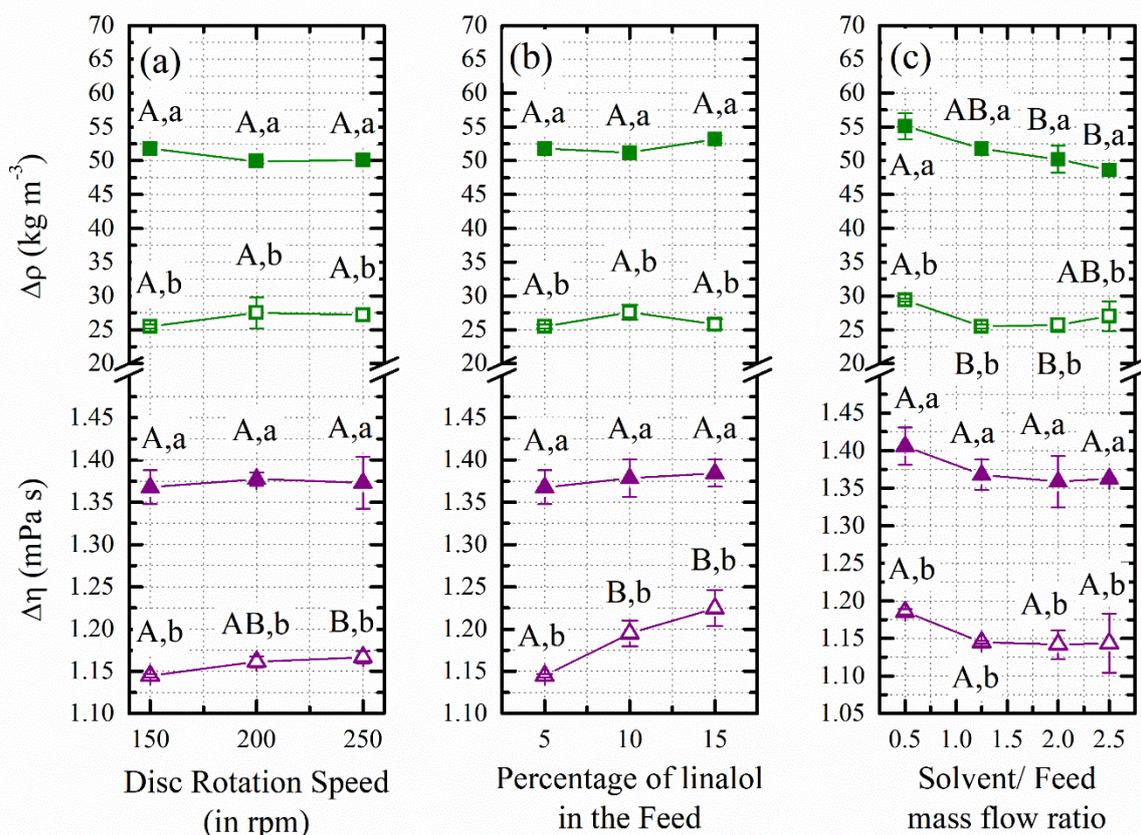
**Fig. 2** - Effect of the variables: (a) DRS, (b) %LF and (c) S/F over the extraction indices:  $\text{---}\circ\text{---}/\text{---}\bullet\text{---}$ , %EXT<sub>LOL</sub> (in %) and  $\text{---}\triangle\text{---}/\text{---}\blacktriangleright\text{---}$ , %EXT<sub>LIM</sub> (in %); (empty symbol) ethanol as the solvent with 30% water (by mass); (full symbol) ethanol as the solvent with 40% water (by mass). The same uppercase letters for the same symbol (empty or full) and the same lowercase letters between empty and full symbols (for the same symbol) indicate no significant difference by Duncan's test ( $P \leq 0.05$ ).



**Fig. 3** - Effect of the variables: (a) DRS, (b) %LF and (c) S/F over the extraction indices:  $-\triangle-/-\blacktriangle-$ , %LE (in %) and  $-\diamond-/-\blacklozenge-$ , %M<sub>SOLV</sub> (in %); (empty symbol) ethanol as the solvent with 30% water (by mass); (full symbol) ethanol as the solvent with 40% water (by mass). The same uppercase letters for the same symbol (empty or full) and the same lowercase letters between empty and full symbols (for the same symbol) indicate no significant difference by Duncan's test ( $P \leq 0.05$ ).



**Fig. 4** - Effect of the variables: (a) DRS, (b) %LF and (c) S/F over the values of:  $\nabla$  (empty symbol) ethanol as the solvent with 30% water (by mass);  $\nabla$  (full symbol) ethanol as the solvent with 40% water (by mass). The same uppercase letters for the same symbol (empty or full) and the same lowercase letters between empty and full symbols (for the same symbol) indicate no significant difference by Duncan's test ( $P \leq 0.05$ ).



**Fig. 5** - Effect of the variables: (a) DRS, (b) %LF and (c) S/F over the experimental values of:  $\square$ — $\square$ —,  $\Delta\rho$  (in  $\text{kg}\cdot\text{m}^{-3}$ ) and  $\triangle$ — $\triangle$ —,  $\Delta\eta$  (in  $\text{mPa}\cdot\text{s}$ ); (empty symbol) ethanol as the solvent with 30% water (by mass); (full symbol) ethanol as the solvent with 40% water (by mass). The same uppercase letters for the same symbol (empty or full) and the same lowercase letters between empty and full symbols (for the same symbol) indicate no significant difference by Duncan's test ( $P \leq 0.05$ ).

Through the calculation of %LE values (Eq. 5), it was possible to compare the composition of linalool in the feed and in the extract stream after the fractionation process, considering only the concentration of limonene and linalool, on a solvent-free basis. According to López-Muñoz and Balderas-López [29], the major traded concentration ranges of oxygenated compounds in citrus essential oils, a procedure industrially known as "fold", are from 2 to 5 for essential oils of lime and mandarin; from 2 to 10 for lemon and grapefruit essential oils and from 2 to 20 for orange essential oil. According to the %LE values presented in Fig. 3, it was determined that the process was able to concentrate linalool from 5% to about 40% (using ethanol with 30% water by mass) and to about 57% (using ethanol with 40% water by mass), which corresponds to concentration processes of almost 7 and 10-fold, respectively.

### III.3.1. Effect of the water content in the solvent

According to Figs. 2, 3, 4 and 5, it is possible to observe that the water content in the solvent significantly affected almost all of the experimental and calculated results. In relation to the extraction indices (Fig. 2), the level of solvent hydration influenced the distribution of the components between the phases and, therefore, the solvent selectivity [3,6,7,9,12,13]. In Fig. 5, an increase in the water content of the solvent led to increased values of the physical properties of the output streams, especially density. The differences between the densities ( $\Delta\rho$ ) and between the dynamic viscosities ( $\Delta\eta$ ) of the output streams (raffinate and extract) were greater for systems where the more hydrated solvent was used (40% water, by mass). It was noted that the water content in the solvent presented almost no influence over the  $\%M_{\text{SOLV}}$  results, for the independent variables studied (DRS,  $\%LF$  and S/F; see Fig. 3).

### III.3.2. Effect of the disc rotation speed

The effect of the disc rotation speed (DRS, in rpm) during the extraction process was studied as a manipulated variable in three conditions: 150, 200 and 250 rpm (nominal values). For these experiments, the feed was composed of  $5.06 \pm 0.01\%$  linalool mass fraction, and the S/F ratio was set at 1.25 (nominal value).

An increase in the DRS promoted a reduction in the droplet size of the dispersed phase (raffinate stream) and, consequently, increased the mass transfer and extraction efficiency [17,18,20,28,30]. However, it was observed that, in general, the DRS exerted almost no influence over the extraction indices (Fig. 2a),  $\%LE$  and  $\%M_{\text{SOLV}}$  values (Fig. 3a). Actually, according to Fig. 2a, it can be seen that a decrease in  $\%EXT_{\text{LOL}}$  values occurred using the solvent with 30% water. This may be due to the axial dispersion phenomenon, since the high rotation speed values may have caused the formation of a vortex, causing changes in the direction of stream flow and, consequently, a reduction in mass transfer [28,31].

Since the variation of DRS almost did not affect the extraction indices, no significant difference was observed in the  $\%LE$  values for both solvents used in this study (Fig. 3a). In this figure is also possible to observe that the  $\%M_{\text{SOLV}}$  values did not undergo significant variations regarding the DRS and the water content of the solvent.

An increase in the DRS had a negative influence on the  $K_{E\cdot a}$  and  $N_{\text{IEO}}$  values, since lower values were estimated for higher DRS values (Fig. 4a), and only values of  $N_{\text{IEO}}$  using the solvent with 30% water could be estimated by the Eq. (12). Since the increase in the DRS caused a decrease in the  $\%EXT_{\text{LOL}}$  values, lower  $K_{E\cdot a}$  values were estimated, which was more significant

using the solvent with 30% water (Fig. 4a). Regarding the  $N_{iEO}$  results, a stronger effect was observed, in which higher DRS values caused lower  $N_{iEO}$  values.

Regarding systems composed of vegetable oil and fatty acids [16,28], in which the raffinate stream provides higher resistance for mass transfer, it has been observed, in general, that an increase in the DRS leads to an increase in the volumetric overall mass transfer coefficients, based on the composition of the raffinate stream ( $K_R \cdot a$ ). Pina et al. [28] observed that an increase in the DRS (over 250 rpm) caused a decrease in  $K_R \cdot a$ , possibly due to axial dispersion. Moreover, Hemmati et al. [20], performing a fractionation study of a system composed of n-butyl acetate-acetone-water, found that the volumetric overall mass transfer coefficients decreased at higher DRS values. These observations are in agreement with the results shown in Fig. 4a.

Concerning the physical properties of the outlet streams, it was possible to observe that variation in the DRS values did not significantly affect the experimental values of  $\Delta\rho$  and  $\Delta\eta$  (Fig. 5a), since almost no influence was observed over the extraction indices (Fig. 2a).

### III.3.3. Effect of the linalool content in the feed stream

The effect of the percentage of linalool in the feed (%LF, Eq. 1) during the performance of the model systems fractionation process was studied as a disturbance variable considering three linalool mass percentages:  $5.06 \pm 0.01$ ,  $9.70 \pm 0.02$  and  $15.00 \pm 0.03\%$ . For these experiments, the DRS value was fixed at 150 rpm and the S/F ratio value was maintained at 1.25 (nominal values).

As shown in Fig. 2b, the increase in %LF influenced almost all extraction indices. For both solvents, an increase in %LF led to an increase in %EXT<sub>LIM</sub>, but did not have a significant effect on %EXT<sub>LOL</sub> values. In fact, an increase in linalool in the system led to an increase in the components and phase solubility [3], resulting in an increase in the %EXT<sub>LIM</sub> (Fig. 2b) and %M<sub>SOLV</sub> (Fig. 3b) values; this corresponds to greater solvent migration to the raffinate stream. Furthermore, it was possible to observe for %LF =  $15.00 \pm 0.03\%$ , the %M<sub>SOLV</sub> values were higher than when the solvent with a higher water content (40%) was used.

A stronger influence of %LF on %EXT<sub>LIM</sub> values was identified in systems in which the solvent with 30% water was used (Fig. 2b), since this solvent presented higher values of the distribution coefficient for limonene [3].

It can be observed that even with an increase in %EXT<sub>LIM</sub> values, %LE increased directly with an increase in %LF (Fig. 3b). This behavior may be due to the larger amount of linalool

in the feed stream and, consequently, a lower amount of limonene. Since an increase in %LF caused an increase in %EXT<sub>LIM</sub>, mainly using the solvent with a lower water content (30%), the estimated values of  $K_E \cdot a$  presented a decrease (Fig. 4b). Moreover, it was observed that the lower the linalool content in the feed (%LF), the greater its concentration in the extract stream (%LE); in other words, more “folds” might be achieved (Fig. 3b).

Apparently, an increase in %LF caused an increase in  $N_{IEO}$ , which was not expected, since the values of  $K_E \cdot a$  decreased (using the solvent with 30% water, see Fig. 4b). However, since the estimation of  $N_{IEO}$  was possible in only two conditions (%LF =  $5.06 \pm 0.01\%$  and  $9.70 \pm 0.02\%$ ), the influence of %LF over  $N_{IEO}$  could not be defined.

According to Fig. 5b, an increase in %LF caused an increase in  $\Delta\eta$ , when the solvent with 30% water was used, possibly due to the significant increase in %EXT<sub>LIM</sub> (Fig. 2b), which led to an increase in the dynamic viscosity of the extract stream.

#### **III.3.4. Effect of the solvent to feed mass flow ratio**

The effect of the solvent to feed mass flow ratio (S/F) during the extraction process was studied as a manipulated variable in four conditions: 0.5, 1.25, 2.0 and 2.5 (nominal values). For these experiments, the DRS was held at 150 rpm (nominal value) and the feed was composed of  $5.06 \pm 0.01\%$  linalool (mass fraction).

According to the results shown in Fig 2c, an increase in the S/F ratio resulted in an increase in the %EXT<sub>LOL</sub> and %EXT<sub>LIM</sub> values, reaching a maximum of about 100% for %EXT<sub>LOL</sub> using the solvent with a lower water mass percentage (30%) and higher S/F ratio (2.5, nominal value). As previously observed in the computational study performed by Romero et al. [22], it was possible to achieve the maximum %EXT<sub>LOL</sub> using an S/F ratio of 1.8 when 1,2-butanediol was used as the solvent. Arce et al. [21] also studied the linalool and limonene separation process by a computational approach, showing %EXT<sub>LOL</sub> values as a function of the S/F ratio for three different solvents. The authors found that, in fact, an increase in the S/F ratio results in higher values of %EXT<sub>LOL</sub>.

Indeed, an increased amount of solvent in the extraction process affected the %EXT<sub>LOL</sub> and %EXT<sub>LIM</sub> values, leading to increased extraction of linalool and limonene. Since limonene was present as the major component of the model system, an increase in %EXT<sub>LIM</sub>, even small, results in a significant increase in the composition of the terpenic hydrocarbons in the extract phase. Due to this fact, it can be seen that an increase in the S/F ratio led to a decrease in %LE

(Fig. 3c). Arce et al. [21], evaluated the relationship between %LE and S/F and found that an increase in S/F caused a decrease in %LE values.

In Fig. 3c, it is possible to see that the higher the S/F ratio used, the lower the %M<sub>SOLV</sub> values; and that no significant differences were observed for both solvents. This behavior is in agreement with the equilibrium data presented in a previous study [3], in which a greater amount of solvent was associated with less migration of the solvent to the raffinate phase.

In addition to the effects already described related to the strong effect of the S/F ratio on %M<sub>SOLV</sub> and on the extraction indices (%EXT<sub>LOL</sub> and %EXT<sub>LIM</sub>), it can be inferred that the mechanical drag of the streams may have also contributed, since the high solvent flow may have dragged the raffinate stream to the bottom of the equipment, where the extract stream was collected.

In relation to K<sub>E</sub>·a values, in general, an increase in S/F led to an increase in K<sub>E</sub>·a (Fig. 4c), since a greater amount of linalool was extracted (Fig. 2c). Torab-Mostaedi and Asadollahzadeh [32] performed the fractionation study of toluene–water–acetone system. They found that an increase in the continuous phase (solvent) led to an increase in the volumetric overall mass transfer coefficient (K<sub>OC</sub>·a).

In Fig. 4c, it is also possible to see that the estimation of N<sub>tEO</sub> was only possible for values of S/F greater than or equal to 1.25 for the solvent with 30% water, and for values of S/F greater than or equal to 2.0 for the solvent with 40% water. According to Geankoplis [14], when the solvent flow is too low, a limit in the process occurs. In this case, an infinite number of theoretical stages is required, or a number of N<sub>tEO</sub> tending to zero, making this estimation unfeasible. When the estimation of N<sub>tEO</sub> is impossible in a specific solvent flow, this flow is called “minimum solvent flow”.

The behavior observed for N<sub>tEO</sub> relating to S/F ratio variation (Fig. 4c) was the same as that observed for %LE values (Fig 3c), such that an increase in S/F caused a decrease in N<sub>tEO</sub> and %LE, even with an increase in %EXT<sub>LOL</sub> and K<sub>E</sub>·a. Thus, using the solvent with a higher water content (40%), higher N<sub>tEO</sub> values were estimated.

An increase in S/F caused a small decrease in Δρ, but had no significant influence on Δη values (Fig. 5c). The decrease in the difference between the densities of the raffinate and extract streams may be due to the huge increase in the extraction indices when the S/F ratio increased (Fig. 2c), making the experimental densities of the streams more similar.

### III.3.5. Fractionation of Crude Orange Essential Oil

The COEO was used as feed stream to provide the separation of terpenes and oxygenated compounds. As previously mentioned, the composition of the raw-material was already determined in a previous study [3], in which the oxygenated compound fraction was composed of octanal, nonanal, citronellal, linalool, octanol, undecanal, neral,  $\alpha$ -terpineol, dodecanal and geranial, with linalool being the major representative compound; the terpene fraction was composed of  $\alpha$ -pinene, limonene, germacrene, caryophyllene and valencene, with limonene being the major representative component. The composition of the COEO used in the fractionation experiments was  $98.73 \pm 0.02\%$  terpenes and  $1.27 \pm 0.02\%$  oxygenated compounds [3].

Once important changes were not observed with the variation of the DRS, as discussed in section 3.2, the value of this variable was fixed at 150 rpm. According to the results from the model systems, the use of  $S/F = 1.25$  provided acceptable values of  $\%EXT_{LIM}$ ,  $\%EXT_{LOL}$ ,  $\%LE$  and low  $\%M_{SOLV}$ , thereby, the variable  $S/F$  was fixed at 1.25. In relation to the water content in the solvent, the two levels of hydration, 30 and 40%, were used in the fractionation process of the COEO once this variable exhibited significant effect on the process performance.

The experimental indices and calculated parameters obtained from the fractionation of COEO in PRDC using solvents composed of ethanol with 30 and 40% water content (in mass) are presented in Table 2. As evidenced in Table 2, increases in water content in the solvent led to decreases in the extraction indices, but also to increases in the concentration of oxygenated compounds in the extract, as observed in the model systems. Additionally, almost no differences were observed in the migration of solvent to the raffinate stream, which presented values very similar to those obtained from the model systems. The differences between the densities and between the viscosities of the output streams also presented values very close to those determined by the model systems.

Once the COEO presented a lower content of oxygenated compounds than the model mixtures used as the feed stream, the extraction indices, such as  $\%EXT_{LIM}$  and  $\%EXT_{LOL}$ , were lower than the values calculated for model mixtures. However, more folds were reached (10-fold using solvent with 30% water content and 15-fold using solvent containing 40% water). Once the increase in  $\%LF$  led the increase of  $\%LE$  (Fig. 3b), it was already expected that for a  $\%LF = 1.27\%$ , the  $\%LE$  values were lower. In the model system, the decrease in  $\%LF$  caused an increase in  $K_E \cdot a$ , but for  $\%LF = 1.27\%$  the calculated  $K_E \cdot a$  was lower than for  $\%LF = 5\%$ , for both solvents. This may be due to the complexity of the COEO composition, which makes

the calculation of  $K_E \cdot a$  and  $N_{tEO}$  much more difficult. However, the estimation of  $N_{tEO}$  was possible to systems with COEO using solvent containing 40% water and  $S/F = 1.25$ , may be due to the low concentration of oxygenated compounds in the feed and, therefore, in the output streams. In Fig. 4b, regarding model systems is possible to observe that the estimation of  $N_{tEO}$  (for solvent containing 30% water) was not possible for  $\%LF = 15\%$ . Therefore, it is possible that the estimation of  $N_{tEO}$  of model systems using solvent containing 40% water could be achieved with lower  $\%LF$  values.

**Table 2:** Experimental and calculated results from the fractionation of crude orange essential oil (COEO) using PRDC.

Water content in the solvent	%EXT <sub>LOL</sub>	%EXT <sub>LIM</sub>	%LE	%M <sub>SOLV</sub>	Folds	N <sub>TEO</sub>	$K_E \cdot a \times 10$ (kg <sub>oxig</sub> ·s <sup>-1</sup> ·m <sup>-3</sup> ·[kg <sub>oxig</sub> ·kg <sub>extract</sub> <sup>-1</sup> ] <sup>-1</sup> )	Δρ (kg·m <sup>-3</sup> )	Δη (mPa·s)
30%	55 ± 3 <sup>A</sup>	4.5 ± 0.2 <sup>A</sup>	14 ± 2 <sup>A</sup>	2.47 ± 0.09 <sup>A</sup>	10.7 ± 0.5 <sup>A</sup>	1.5 ± 0.1 <sup>A</sup>	4.8 ± 0.1 <sup>A</sup>	25.47 ± 0.09 <sup>A</sup>	1.079 ± 0.008 <sup>A</sup>
40%	28 ± 1 <sup>B</sup>	1.48 ± 0.02 <sup>B</sup>	22 ± 1 <sup>B</sup>	2.5 ± 0.2 <sup>A</sup>	15.1 ± 0.3 <sup>B</sup>	1.4 ± 0.2 <sup>A</sup>	3.2 ± 0.9 <sup>B</sup>	49 ± 2 <sup>B</sup>	1.28 ± 0.01 <sup>B</sup>

The same uppercase letters for the same column indicates no significant difference by Duncan's test ( $P \leq 0.05$ ).

### III.4. Conclusions

The fractionation process of citrus essential oil model systems composed of limonene and linalool, and of real systems composed of orange crude essential oil (OCEO), was possible using a PRDC, operating continuously and in a countercurrent configuration, in which mixtures of ethanol and water were used as the solvent. In fact, oxygenated compounds-rich phases were obtained using both solvents. For the model systems, the highest concentration of linalool in the extract, on a solvent-free basis (%LE), was close to 7-fold greater using the solvent containing 30% water and close to 10-fold greater using the solvent containing 40% water. For real systems, the %LE results were 10-fold greater using solvent containing 30% water and 15-fold greater using solvent containing 40% water. These ranges correspond to the ones adopted by the market.

In all experiments, the  $\Delta\rho$  experimental values were sufficient to provide mechanical separation between the phases into the top and bottom separation regions of the equipment and, consequently, the stability of the process. Moreover, none of the studied variables presented a notable effect on the physical properties differences of the output streams.

In general, all the studied variables affected the fractionation process of the model mixtures. The disc rotation speed (DRS), was not a good choice as a manipulated variable since its variation did not strongly affect the process. An increase in DRS actually led to a decrease in linalool extraction (%EXT<sub>LOL</sub>) and a decrease in the overall volumetric mass transfer coefficient ( $K_E \cdot a$ ) of linalool.

The solvent to feed mass flow ratio (S/F) directly affected the process, and was a good alternative choice for a manipulated variable. An increase in S/F caused an increase in %EXT<sub>LOL</sub>, achieving a maximum value of almost 100% using the solvent containing 30% water (by mass) when the S/F ratio was 2.5. However, high S/F values were responsible for increasing the diluent extraction (%EXT<sub>LIM</sub>) and, consequently, led to a lower concentration of linalool in the extract, on a solvent-free basis (%LE), as well as lower values of mass transfer units ( $N_{iEO}$ ).

The water content in the solvent also exerted a strong influence on the process. For both model and real systems, almost all indices studied showed significant differences when the water content in the solvent was changed. For all variables, an increase in the amount of water in the solvent caused a decrease in %EXT<sub>LOL</sub>, %EXT<sub>LIM</sub> and  $K_E \cdot a$ , but caused an increase in %LE. For model systems, higher %LE values were found using an S/F ratio equal to 0.5 and a solvent with higher water content (40% by mass).

The linalool concentration in the feed (%LF), as a disturbance variable, affected the process significantly. An increase in the solute (linalool) content in the feed stream caused more extraction of the diluent (limonene), more solvent migration to the raffinate stream (%M<sub>SOLV</sub>) and lower K<sub>E</sub>·a values. However, an increase in %LF led to an increase in %LE, since a higher linalool content was available in the system. In the case of COEO, which presented a low concentration of oxygenated compounds (%LF = 1.27%) the %LE values were lower than for %LF = 5%, which was expected.

In general, the behavior observed for model systems was also noted in real systems. The water content in the solvent presented greater effects on the fractionation process for all systems studied.

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# CHAPTER IV: Fractionation of acid lime essential oil using ethanol/water mixtures – Effect of the process on the aroma profile



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## Fractionation of acid lime essential oil using ethanol/water mixtures: Effect of the process on the aroma profile



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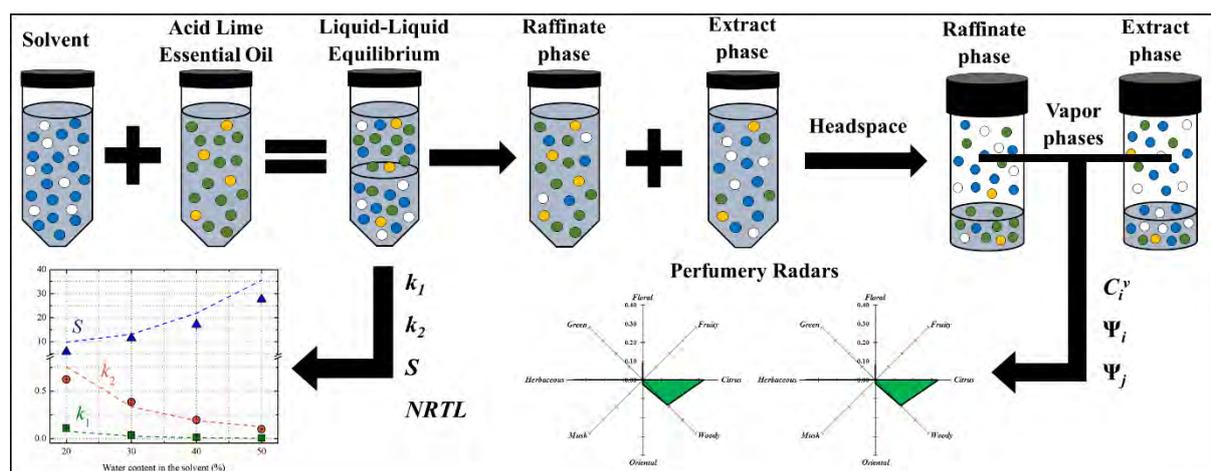
NRTL

### ABSTRACT

This study aims to separate aroma-active components of the crude *Citrus latifolia* essential oil (EO) from the unstable terpene hydrocarbons using ethanol/water mixtures through liquid–liquid equilibrium (LLE) and to evaluate the aroma profiles of the crude EO and the LLE phases. For this purpose, the liquid compositions of the crude EOs and the LLE phases were found by gas chromatography analysis. The compositions of the liquid phases were predicted using the NRTL model and compared to the experimental data. Afterwards, the concentrations of the components in the vapour phases above the liquid mixtures were obtained by headspace analysis and the odour intensity of each component was estimated using the Stevens' power law concept. Finally, the classification into olfactory families was evaluated through the Perfumery Radar methodology. The solvent extraction technique made it possible to obtain extract phases enriched in citral and poor in monoterpenes, with aromas profiles similar to that of the crude EO and classified as herbaceous and citrus scent, with floral, woody, and oriental nuances. The extract phase obtained from ethanol with 50% water was found to be a promising fraction for industrial applications. Furthermore, the results proved that the NRTL parameters can be efficiently used to predict the compositions of the phases from the LLE.

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## IV. Graphical abstract



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## IV. Highlights

- Fractionation of crude acid lime essential oil using ethanol/water mixtures.
- Extract phases were enriched in aroma-active components.
- Predicted compositions of liquid phases fitted well with the experimental data.
- Aroma-active components were separated from terpenes, keeping the original acid lime essential oil odor.
- The water content in the solvent did not affect the aroma profile of the phases from the liquid–liquid equilibrium.

### IV.1. Introduction

The essential oil (EO) extracted from acid lime (*Citrus latifolia* Tanaka) peel is extensively applied in the beverage industry as a flavoring agent for soft drinks, being one the main constituents of cola flavor [1]. It is also widely used in ice creams, confectionery, and bakery formulations, as well as to mask unpleasant odors in pharmaceutical and cosmetic products [2]. As a citrus EO, the acid lime EO is composed of volatile (monoterpene hydrocarbons and their oxygenated derivatives) and non-volatile (waxes, pigments, fatty acids, carotenoids, etc.) fractions [3,4].

The oxygenated terpene derivatives, which appear as minor fractions in the acid lime EO, are reported as its main aroma-active constituents [2,3,5] besides being the most stable group of components [6]. This fraction is mainly composed of the isomeric aldehydes neral and geranial (4–6%) [7], commonly called citral, which make an enormous contribution to the lemon-like aroma [8–12]. For this reason, the citral content in the lemon/lime EO is an important parameter for the establishment of its quality and commercial value [13]. On the other hand, the monoterpene hydrocarbons, which represent about 95% of the volatile fraction of acid lime EO, are unsaturated compounds easily decomposed by heat, light, and oxygen, compromising its aroma quality [3,12,14,15].

A common industrial practice is to isolate the oxygenated compounds by reducing the terpenes content in the EO (a procedure called deterpenation) in order to avoid these degradation reactions. From this process, the stability of the EO is increased [2,16] as well as its solubility in water, ethanol, and other solvents used in food technology [14]. Vacuum distillation and/or solvent extraction are the deterpenation techniques applied at large scale [4,14]. The fractionated EO obtained by solvent extraction possibly presents better sensory

quality than that isolated by distillation, since more volatile aliphatic components (associated with the fresh and juicy citrus character) may be preserved [1]; however this statement has not been proved so far. Furthermore, previous studies demonstrated that hydroalcoholic solvents can be used to efficiently separate key odorant components, such as citral, from lemon/lime EO model mixtures [2].

Thus, considering the impact of the acid lime EO in the industry and the absence of scientific studies focused on the fractionation of the crude EO, this study aims to experimentally determine the liquid–liquid equilibrium (LLE) data of systems composed of crude acid lime EO, ethanol, and water at  $T = (298.2 \pm 0.1)$  K and to predict the compositions of the LLE phases using the non-random two-liquid model [17] parameters from the literature [2]. Moreover, the impact of the fractionation process on the aroma profile of the acid lime EO and LLE phases was evaluated by estimating the odor intensity of the components in the vapor phases using the Stevens' power law concept [18] and by the construction of Perfumery Radars (PRs) [19].

## IV.2. Material and methods

### IV.2.1. Chemicals

*C. latifolia* EO was industrially extracted from the peel of acid lime fruits by the cold pressing technique. The crude acid lime EO was kindly donated by Louis Dreyfus Company (Bebedouro, SP, Brazil). Medicinal air, helium, hydrogen, and synthetic air were acquired from Air Liquide (Portugal). The chemical names, empirical formulas, CAS numbers, supplier and experimental purities, and the source of the materials used in this study are displayed in Table 1. The properties of the standards are shown in Table 2, namely the molar masses ( $M_i$ ) [20], vapor pressures at  $T = 298.2$  K ( $P_i^{sat}$ ) [20–22], odor detection thresholds ( $ODT_i$ ) [23], power law exponents ( $n_i$ ) [24], and their classification into the olfactory families [9,22,25,26].

### IV.2.2. Liquid–liquid and vapor–liquid equilibria

Different systems containing hydroalcoholic solvents (ethanol with 20, 30, 40, and 50% water by mass) and EO with a mass ratio of 1:1 were prepared. Systems were maintained at  $T = (298.2 \pm 0.1)$  K for 20 h to stabilize the LLE. After that, two homogeneous and well-formed phases were obtained: the terpene-rich phase (raffinate) and the solvent-rich phase (extract). Samples from both phases were collected separately using syringes, and their compositions

were determined according to methodology presented in Section 2.3.1. The LLE assays were performed in triplicate.

The vapor–liquid equilibrium (VLE) was attained by placing 1 mL of the liquid sample (crude acid lime EO or the phases from the LLE) in a 20 mL closed-cap headspace vial, which was maintained at  $T = (298.2 \pm 0.1)$  K for 20 h before the headspace analysis (Section 2.3.2).

**Table 1:** Chemical names, empirical formulas, CAS numbers, mass fraction purities, and provenance of the materials.

Material	Chemical name	Empirical formula	CAS registry number	Supplier purity <sup>a</sup>	Experimental purity <sup>b</sup>	Source
<i>R</i> -(+)-Limonene	( <i>R</i> )-4-Isopropenyl-1-methyl-1-cyclohexene	C <sub>10</sub> H <sub>16</sub>	5989-27-5	0.970	0.988	Sigma-Aldrich, USA
(-)- $\beta$ -pinene	(1 <i>S</i> ,5 <i>S</i> )-6,6-Dimethyl-2-methylenebicyclo[3.1.1]heptane	C <sub>10</sub> H <sub>16</sub>	18172-67-3	0.990	0.999	Fluka, Switzerland
$\gamma$ -Terpinene	1-Isopropyl-4-methyl-1,4-cyclohexadiene	C <sub>10</sub> H <sub>16</sub>	99-85-4	0.970	0.977	Sigma-Aldrich, USA
(-)- $\alpha$ -Pinene	(1 <i>S</i> ,5 <i>S</i> )-2,6,6-Trimethylbicyclo[3.1.1]hept-2-ene	C <sub>10</sub> H <sub>16</sub>	7785-26-4	0.980	0.990	Sigma-Aldrich, USA
Citral	3,7-Dimethyl-2,6-octadienal	C <sub>10</sub> H <sub>16</sub> O	5392-40-5	0.960	0.990	Sigma-Aldrich, USA
Linalool	( $\pm$ )-3,7-Dimethyl-1,6-octadien-3-ol	C <sub>10</sub> H <sub>18</sub> O	78-70-6	0.970	0.992	Sigma-Aldrich, USA
$\alpha$ -Terpineol	2-(4-Methylcyclohex-3-en-1-yl)propan-2-ol	C <sub>10</sub> H <sub>18</sub> O	98-55-5	0.900	0.920	Sigma-Aldrich, USA
Geraniol	<i>trans</i> -3,7-Dimethyl-2,6-octadien-1-ol	C <sub>10</sub> H <sub>18</sub> O	106-24-1	0.980	0.920	Sigma-Aldrich, USA
Decanal	Decyl aldehyde	C <sub>10</sub> H <sub>20</sub> O	112-31-2	0.950	0.900	Fluka, Switzerland
Ethanol	Ethyl alcohol	C <sub>2</sub> H <sub>6</sub> O	64-17-5	0.998	0.999	Chem-Lab, Belgium
Water		H <sub>2</sub> O	7732-18-5			

<sup>a</sup> The reagents were used without further purification;

<sup>b</sup> Experimentally determined by GC-FID analysis, given as mass fraction.

**Table 2:** Chemical composition of the crude acid lime essential oil (%  $w_i$ , in mass percentages), molar masses ( $M_i$ , in  $\text{g}\cdot\text{mol}^{-1}$ ), vapor pressures at  $T = 298.2\text{ K}$  ( $P_i^v$ , in Pa), vapor concentrations ( $C_i^v$ , in  $\text{g}\cdot\text{m}^{-3}$ ) at  $T = 298.2\text{ K}$  and  $p = 1 \times 10^5\text{ Pa}^*$ , odor detection thresholds in air ( $ODT_i$ , in  $\text{g}\cdot\text{m}^{-3}$ ), power law exponents ( $n_i$ ), odor intensities ( $\Psi_i$ ), and olfactory family classification of each component.

Component ( $i$ )	% $w_i$	$M_i/\text{g}\cdot\text{mol}^{-1}$	$P_i^v/\text{Pa}$	$C_i^v/\text{g}\cdot\text{m}^{-3}$	$ODT_i^{**}$	$n_i^{***}$	$\Psi_i$	Olfactory Family <sup>****</sup>	
								Primary	Secondary
Water		18.02	3172 <sup>a</sup>					Odorless	
Ethanol		46.07	7901 <sup>a</sup>		$3.74 \times 10^{-2}$	0.58		Alcohol	
<i>Terpenes</i>	$92.2 \pm 0.3$	$136.2$	-	$8.8 \pm 0.2$					
$\alpha$ -Pinene	$2.3 \pm 0.5$	136.2	633.3 <sup>a</sup>	$1.21 \pm 0.04$	$2.88 \times 10^{-4}$	0.49	$60 \pm 2$	Herbaceous	Woody
$\beta$ -Pinene	$13.4 \pm 0.1$	136.2	390.6 <sup>a</sup>	$2.31 \pm 0.06$	$8.75 \times 10^{-3e}$	0.35	$7.0 \pm 0.2$	Woody	Oriental
Limonene	$61.4 \pm 0.3$	136.2	206.4 <sup>a</sup>	$4.2 \pm 0.1$	$5.60 \times 10^{-4}$	0.37	$27.1 \pm 0.9$	Citrus	
$\gamma$ -Terpinene	$15.1 \pm 0.2$	136.2	144.9 <sup>a</sup>	$1.13 \pm 0.07$	$2.00 \times 10^{-3f}$	0.35	$9.2 \pm 0.6$	Citrus	Herbaceous
<i>Oxygenated compounds</i>	$7.8 \pm 0.1$	$154.3$		$0.102 \pm 0.003$					
Decanal	$0.1 \pm 0.1$	156.3	13.73 <sup>a</sup>	$0.001 \pm 0.001$	$5.67 \times 10^{-5}$	0.39	$3.1 \pm 0.3$	Oriental	Floral
Linalool	$0.4 \pm 0.1$	154.2	21.33 <sup>a</sup>	$0.003 \pm 0.001$	$1.73 \times 10^{-5}$	0.35	$5.8 \pm 0.2$	Floral	
Neral	$2.0 \pm 0.2$	152.2	12.17 <sup>c</sup>	$0.045 \pm 0.001$	$2.78 \times 10^{-5g}$	0.32	$10.6 \pm 0.3$	Floral	Citrus
$\alpha$ -Terpineol	$0.4 \pm 0.1$	154.3	5.64 <sup>a</sup>	$0.002 \pm 0.001$	$1.09 \times 10^{-4}$	0.35	$2.8 \pm 0.1$	Floral	Woody
Geranial	$4.2 \pm 0.4$	152.2	12.17 <sup>c</sup>	$0.050 \pm 0.002$	$2.78 \times 10^{-5g}$	0.31	$10.2 \pm 0.5$	Floral	Citrus
Geranyl acetate	$0.4 \pm 0.1$	196.3	6.17 <sup>b</sup>		$1.47 \times 10^{-2}$	0.35		Floral	Green
Geraniol	$0.3 \pm 0.1$	154.3	4 <sup>c</sup>	$0.002 \pm 0.001$	$7.10 \times 10^{-7}$	0.36	$7.0 \pm 0.5$	Floral	
Nerol	$0.1 \pm 0.1$	154.3	1.77 <sup>d</sup>		$5.67 \times 10^{-5}$	0.35		Floral	

\* Standard uncertainties  $u$  are  $u(T) = 0.1\text{ K}$ ,  $u(p) = 1 \times 10^3\text{ Pa}$ ,  $u(\%w)$  presented after the mass percentage value,  $u(C_i^v)$  after the vapor concentration value, and  $u(\Psi_i)$  after the odor intensity value;

\*\* Geometric averages from van Gemert [23];

\*\*\* From Devos et al. [24];

\*\*\*\* Based in Brechbill [9], Parchem [22], The Good Scents Company [25] and Cameo Chemicals [26];

<sup>a</sup> Experimental values from SRC HysProp Database [20];

<sup>b</sup> Estimated values from NCBI PubChem Database [21], by Antoine equation;

<sup>c</sup> Extrapolated value from SRC HysProp Database [20];

<sup>d</sup> Extrapolated value from Parchem [22];

<sup>e</sup> Geometrically averaged from van Gemert [23] and the experimental value evaluated in this study ( $8.60 \times 10^{-3}\text{ g}\cdot\text{m}^{-3}$ );

<sup>f</sup> Geometrically averaged from van Gemert [23] and the experimental value evaluated in this study ( $1.59 \times 10^{-3}\text{ g}\cdot\text{m}^{-3}$ );

<sup>g</sup> Geometrically averaged from van Gemert [23] and the experimental value evaluated in this study ( $1.93 \times 10^{-5}\text{ g}\cdot\text{m}^{-3}$ ).

### IV.2.3. Chemical analysis

#### IV.2.3.1. Liquid samples

The chemical profiles of the volatile fraction of the crude acid lime EO and the LLE phases were assessed by gas chromatography (GC) using a Varian CP-3800 equipped with a split/splitless injector coupled with mass spectrometry (MS) and a capillary column DB-FFAP (Agilent, USA) (0.25  $\mu\text{m}$  film thickness, 30 m  $\times$  0.25 mm i.d.) under the same conditions as used by Gonçalves et al. [6]. The injector temperature was set as 523.2 K. Samples were diluted in 1-propanol (1:1) and injected (0.1  $\mu\text{L}$ ) with a split ratio of 50:1. Liquid sampling and injection were performed manually using a syringe from SGE (Australia). The carrier gas (He N60) flow was maintained at 1.56 mL/min. The oven temperature program was initially set at 375.2 K and then raised to 513.2 K at a rate of 8 K/min and held isothermally for 1 min. The mass spectra scanning ranged from 80 to 500 m/z and the source ionization energy was 70 eV. The mass spectra of the volatile components were compared with the spectral libraries [NIST98 (USA) and database of Flavors and Fragrances of Natural and Synthetic Compounds 2 (John Wiley & Sons, USA)] and with the retention times of the pure compounds injected under the same GC-MS conditions.

The quantification of the volatile components was performed according to Gonçalves et al. [6] using a Varian CP-3800 equipped with a split/splitless injector, flame ionization detector (GC-FID), and a capillary DB-FFAP column. The oven temperature program was initially set at 373.2 K, then raised to 513.2 K at a rate of 8 K/min, and held isothermally for 1 min. The carrier gas (He N60) was maintained at a constant flow rate of 1.13 mL/min and the detector temperature was set at 523.2 K. The quantification of the components was determined by an external standard method. The GC-FID analyses were carried out in triplicate for the crude acid lime EO, and in duplicate for each LLE phase.

#### IV.2.3.2. Vapor samples

The concentrations in the vapor phase above the liquid (crude acid lime EO or the phases from the LLE) ( $C_i^v$ ) from the VLE were evaluated by static headspace gas chromatography (HS-GC) using a Varian CP-3800 equipped with a split/splitless injector, flame ionization detector, and capillary DB-FFAP column. The gas samples (0.2 mL) were injected using a split ratio of 50:1 for the crude EO and raffinate phases and 150:1 for the extract phases. The carrier gas, oven temperature program, and injector and detector temperatures were the same as those

used for the analysis of the liquid phases. Gas sampling and injection were done using a gastight syringe from SGE (Australia) installed in an automatic headspace sampler HT250D by HTA SrL. The quantification of the components was achieved by an external standard method. For the crude acid lime EO, three headspace vials were prepared for the VLE, while two vials were prepared for each LLE phase from the triplicate (data shown in Table 3), totalizing six vials for each LLE phase sample (for the same solvent).

#### IV.2.4. Prediction of the liquid phases' composition

The thermodynamic parameters of NRTL estimated by Koshima et al. [2] were used to predict the compositions of the phases from the LLE. For that, the components identified in the crude acid lime EO were classified into two pseudo-components or groups, terpenes (1) and oxygenated compounds (2), using the average molar masses indicated in Table 2. The partitioning (or distribution coefficients) of the terpenes and the oxygenated compounds between the phases ( $k_i$ ) was calculated by Eq. (1). The solvent selectivity values for the oxygenated compounds ( $S$ ) were determined by Eq. (2).

$$k_i = \frac{w_i^{EP}}{w_i^{RP}} \quad (1)$$

where  $w$  is the mass fraction of component  $i$  [terpenes (1) or oxygenated compounds (2) group],  $EP$  is the extract phase, and  $RP$  is the raffinate phase.

$$S = \frac{k_2}{k_1} \quad (2)$$

For the prediction procedure, the interaction parameters published by Koshima et al. [2] for limonene were used for the prediction of the compositions of the terpenes group. In the same way, the interaction parameters for citral were used for the estimation of the compositions of the oxygenated compounds group. This approach was already applied by Gonçalves et al. [6], who prepared a citrus model system composed of limonene, linalool, ethanol, and water at  $T = 298.2$  K to adjust the parameters of the NRTL and UNIQUAC models and successfully used the parameters of limonene representing the terpenes group and linalool (the main oxygenated compound in orange EO) representing the oxygenated compounds group to predict the compositions of the LLE phases.

The predictive method comprises flash calculations for the experimental overall composition of the tie-lines (Table 3), as suggested by Stragevitch and D'Avila [27]. The deviation between the experimental and predicted compositions was calculated by Eq. (3).

$$\Delta w = \sqrt{\frac{\sum_{n=1}^N \sum_{i=1}^K \left[ \left( w_{i,n}^{RP,exp} - w_{i,n}^{RP,pred} \right)^2 + \left( w_{i,n}^{EP,exp} - w_{i,n}^{EP,pred} \right)^2 \right]}{2NK}} \quad (3)$$

where  $N$  and  $K$  are the total number of tie-lines and components, respectively,  $w$  is the mass fraction of component  $i$ ,  $n$  is the tie-line, and *exp* and *pred* refer to the experimental and predicted compositions, respectively.

#### IV.2.5. Odor intensity

The  $C_i^v$  values were converted into perceived sensations using the psychophysical Stevens' power law model [18]. This model is a non-linear relation between the strength of some stimulus and its sensory degree, based on the principle that equal stimulus ratios tend to produce the same sensation ratios raised to an exponent [18]. Therefore, the odor intensity calculated by Stevens' power law model [ $\Psi_i$ , Eq. (4)] describes the ratio between the vapor concentration of the component  $i$  ( $C_i^v$ , in  $\text{g} \cdot \text{m}^{-3}$ ) and its odor detection threshold in the air ( $ODT_i$ , in  $\text{g} \cdot \text{m}^{-3}$ ), raised to its power exponent ( $n_i$ ).

$$\Psi_i = \left( \frac{C_i^v}{ODT_i} \right)^{n_i} \quad (4)$$

where  $ODT_i$  is the minimum concentration of the component  $i$  that can be perceived by the human nose in the air [28]. Despite the compilations available in the literature for  $ODT$  values, they remain incomplete due to the existing large number of compounds. In addition, for some components, only one  $ODT$  value is available. This is the case for  $\gamma$ -terpinene,  $\beta$ -pinene, and citral (neral and geranial mixture), which are important components present in the acid lime EO, for which  $ODT$ s were experimentally measured in this study.

**Table 3:** Experimental liquid–liquid equilibrium data for systems composed of crude acid lime essential oil, represented by terpenes (1) + oxygenated compounds (2) + ethanol (3) + water (4) in mass percentages (%w) at the temperature  $T = 298.2$  K and pressure  $p = 1 \times 10^5$  Pa.<sup>a</sup>

%w <sub>4,s</sub> <sup>b</sup>	Overall Composition				Upper Phase				Bottom Phase			
	%w <sub>1</sub>	%w <sub>2</sub>	%w <sub>3</sub>	%w <sub>4</sub>	%w <sub>1</sub>	%w <sub>2</sub>	%w <sub>3</sub>	%w <sub>4</sub>	%w <sub>1</sub>	%w <sub>2</sub>	%w <sub>3</sub>	%w <sub>4</sub>
19.9 ± 0.5	46.3 ± 0.3	3.5 ± 0.1	40.2 ± 0.5	10.0 ± 0.5	9.5 ± 0.5	2.8 ± 0.5	68.8 ± 0.5	18.9 ± 0.3	85.2 ± 0.5	4.3 ± 0.3	9.9 ± 0.5	0.6 ± 0.1
	46.5 ± 0.3	3.5 ± 0.1	40.1 ± 0.5	9.9 ± 0.5	9.0 ± 0.2	2.7 ± 0.1	69.3 ± 0.5	19.0 ± 0.4	84.9 ± 0.5	4.4 ± 0.2	10.0 ± 0.3	0.7 ± 0.1
	46.5 ± 0.3	3.5 ± 0.1	40.0 ± 0.5	10.0 ± 0.5	8.9 ± 0.5	2.7 ± 0.5	69.3 ± 0.5	19.2 ± 0.4	84.9 ± 0.5	4.4 ± 0.5	10.0 ± 0.5	0.7 ± 0.1
31.0 ± 0.5	46.8 ± 0.3	3.6 ± 0.1	34.2 ± 0.5	15.4 ± 0.5	87.1 ± 0.5	5.2 ± 0.3	7.3 ± 0.5	0.5 ± 0.1	2.9 ± 0.5	1.8 ± 0.4	64.4 ± 0.5	31.0 ± 0.1
	46.5 ± 0.3	3.5 ± 0.1	34.4 ± 0.5	15.5 ± 0.5	88.3 ± 0.5	5.0 ± 0.3	6.2 ± 0.4	0.5 ± 0.1	3.0 ± 0.4	2.0 ± 0.2	64.0 ± 0.5	31.0 ± 0.5
	46.5 ± 0.3	3.5 ± 0.1	34.5 ± 0.5	15.5 ± 0.5	88.3 ± 0.4	5.0 ± 0.1	6.3 ± 0.1	0.4 ± 0.1	3.0 ± 0.2	2.0 ± 0.4	63.7 ± 0.5	31.3 ± 0.5
42.6 ± 0.5	46.7 ± 0.3	3.6 ± 0.1	29.3 ± 0.5	20.5 ± 0.5	89.3 ± 0.5	5.8 ± 0.1	4.6 ± 0.1	0.4 ± 0.1	1.1 ± 0.5	1.1 ± 0.5	55.7 ± 0.5	42.1 ± 0.5
	46.3 ± 0.3	3.6 ± 0.1	28.8 ± 0.5	21.4 ± 0.5	91.0 ± 0.5	6.0 ± 0.5	2.7 ± 0.4	0.4 ± 0.1	1.1 ± 0.1	1.1 ± 0.1	55.2 ± 0.5	42.6 ± 0.4
	45.8 ± 0.3	3.5 ± 0.1	29.3 ± 0.5	21.3 ± 0.5	90.3 ± 0.5	5.9 ± 0.5	3.4 ± 0.5	0.4 ± 0.1	1.0 ± 0.1	1.2 ± 0.2	55.7 ± 0.5	42.2 ± 0.5
50.5 ± 0.5	46.5 ± 0.3	3.5 ± 0.1	24.8 ± 0.5	25.2 ± 0.5	90.0 ± 0.5	6.2 ± 0.5	3.4 ± 0.5	0.4 ± 0.1	0.4 ± 0.1	0.6 ± 0.1	47.6 ± 0.5	51.4 ± 0.5
	46.8 ± 0.3	3.6 ± 0.1	24.6 ± 0.5	25.0 ± 0.5	90.9 ± 0.5	6.4 ± 0.5	2.3 ± 0.5	0.4 ± 0.1	0.4 ± 0.1	0.6 ± 0.1	47.8 ± 0.5	51.1 ± 0.4
	46.7 ± 0.3	3.6 ± 0.1	24.6 ± 0.5	25.1 ± 0.5	90.6 ± 0.5	6.4 ± 0.5	2.7 ± 0.1	0.3 ± 0.1	0.2 ± 0.1	0.6 ± 0.2	47.2 ± 0.5	51.9 ± 0.5

<sup>a</sup> Standard uncertainties  $u$  are  $u(T) = 0.1$  K,  $u(p) = 1 \times 10^3$  Pa, and  $u(\%w)$  presented after each mass percentage value;

<sup>b</sup> Water mass percentage in the solvent.

#### IV.2.6. Odor detection threshold measurement

The measurement of the  $ODT$  for  $\gamma$ -terpinene,  $\beta$ -pinene, and citral in the air was performed according to Gomes et al. [29] using an Ecoma model T07 olfactometer (Germany) built according to VDI3881 [30] and EN13725 [31] standards. Samples were individually prepared in a 5 L Nanoplan NA gas sampling bag with a PET tube (Olfasense, Germany). A known gas volume of the pure compound was diluted in medicinal air inside the bag, which was maintained for 1 h at  $T = (298.2 \pm 0.1)$  K to provide equilibrium of the gas mixture before the analysis. The measurements were carried out by a panel constituted by four untrained people from the laboratory, two women and two men, 27 to 32 years old, at a controlled room temperature  $T = (298 \pm 1)$  K. The odor detection threshold of the component  $i$  ( $ODT_i$ , in  $\text{g}\cdot\text{m}^{-3}$ ) was calculated by Eq. (5). The experimental conditions for the measurements are summarized in Table 4.

$$ODT_i = \frac{C_i^0}{Z_i^{thr}} \quad (5)$$

$C_i^0$  is the gas concentration of the component  $i$  in the sampling bag (in  $\text{g}\cdot\text{m}^{-3}$ ) and  $Z_i^{thr}$  is its threshold dilution factor, which is calculated by Eq. (6).

$$Z_i^{thr} = 10^M \quad (6)$$

where  $M$  is the arithmetic average of the logarithm of the threshold dilution factors calculated by Eq. (7):

$$M = \frac{\sum_{k=1}^4 \sum_{l=1}^3 \log_{10}(Z_{k,l}^{thr})}{L} \quad (7)$$

$Z_{k,i}^{thr}$  is the threshold dilution factor for panelist  $k$  at the measuring sequence  $l$  [Eq. (8)], and  $L$  is the total number of answers.

$$Z_{k,i}^{thr} = \sqrt{Z_N \cdot Z_{N-1}} \quad (8)$$

$Z_N$  is the dilution of the first positive answer, and  $Z_{N-1}$  is the dilution of the last negative answer (when no odor was detected). The calculation was performed after obtaining two consecutive positive answers ( $Z_N$  and  $Z_{N+1}$ ). The experimental  $ODT_i$  values, together with  $ODT$  values from the literature, are presented in Table 2.

**Table 4:** Experimental conditions used for the olfactory measurements.

Parameter	Valor Set <sup>a</sup>
Dilution step	2 <sup>b</sup>
Dilution range	2.5 – 640
Measuring sequences ( <i>l</i> )	3
Interval between sequences	60 seconds
Number of panelists ( <i>k</i> )	4
Breathing time	2.2 seconds
Air flow rate (inhaling)	1.2 m <sup>3</sup> ·h <sup>-1</sup> (1.5 × 10 <sup>5</sup> Pa)
Operating air	Medicinal air
Inlet gas pressure	3 × 10 <sup>5</sup> Pa
Operating pressure	1.5 × 10 <sup>5</sup> Pa
Room temperature	298 ± 1 K

<sup>a</sup> According to Gomes et al. [29];

<sup>b</sup> Actual dilution ratio is the half of the previous one, in a measuring sequence.

#### IV.2.7. Classification of the crude acid lime essential oil and the phases from the liquid–liquid equilibrium into olfactory families

The crude EO and LLE phases were classified into olfactory families using the PR methodology proposed by Teixeira et al. [19]. This approach considers that the scent of a fragrance mixture is governed by a single odorant with a discriminating stronger sensation (detailed information about the methodology can be found in Teixeira et al. [19,28]).

For the construction of the PRs, each component identified in the liquid phases and quantified in the vapor phases was categorized into primary and secondary olfactory families (Table 2), based on the classifications described by Brechbill [9], CAMEO Chemicals [26], Parchem [22], and The Good Scents Company [25]. The odor intensity of each olfactory family ( $\Psi_j$ ) was calculated by Eq. (9):

$$\Psi_j = \sum_{i=1}^N F_i^j \times \Psi_i \quad (9)$$

where  $j$  is the olfactory family (citrus, woody, oriental, musk, herbaceous, green, or floral),  $i$  is the component belonging to the family  $j$ ,  $N$  is the total number of components in the family  $j$ , and  $F_i^j$  is the weight factor for the component  $i$  in the family  $j$  ( $F_i^j = 0.7$  for the primary family and  $F_i^j = 0.3$  for the secondary family) [19].

#### IV.2.8. Statistical Analysis

The significant differences among the PRs of the crude acid lime EO and the LLE phases, in terms of olfactory families, were evaluated by variance analysis with Duncan's test at a significance level of  $P \leq 0.05$ , using SAS software (version 9.2, SAS Institute, Cary, NC, USA).

### IV.3. Results and discussion

#### IV.3.1. Liquid composition of the crude acid lime essential oil

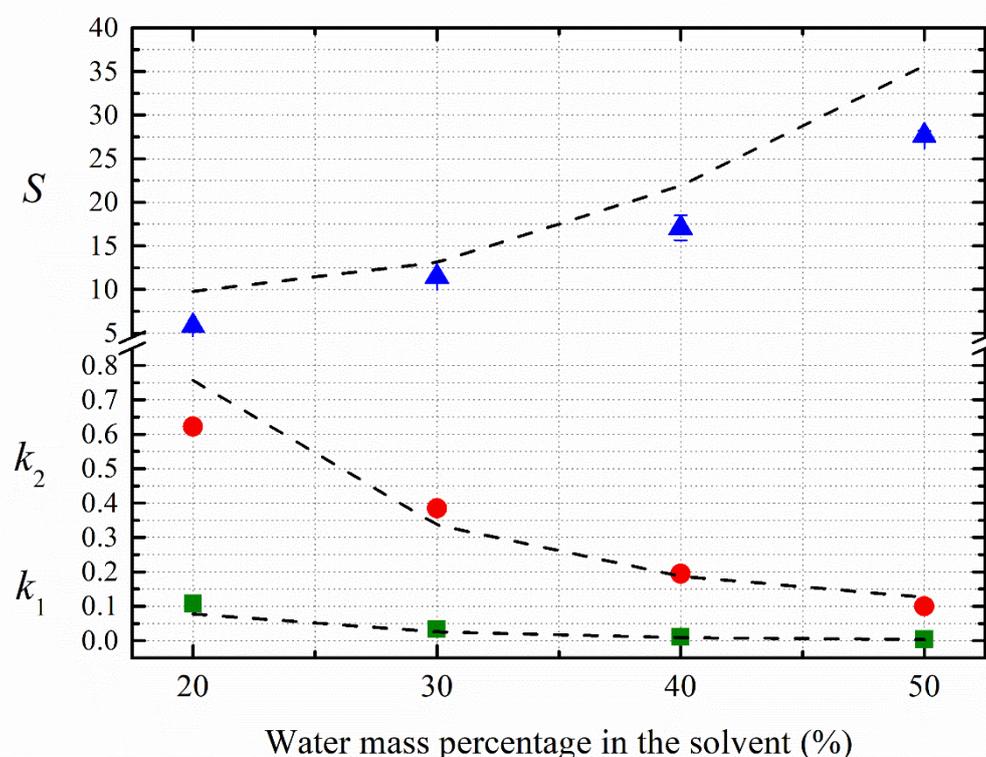
The chemical analysis revealed that the volatile fraction of the crude acid lime essential oil is composed of monoterpene hydrocarbons ( $92.2 \pm 0.3\%$ ) and their oxygenated derivatives ( $7.8 \pm 0.1\%$ ), in mass percentages of the components identified by GC-MS and quantified by GC-FID (Table 2). Limonene was the most abundant monoterpene ( $61.4 \pm 0.3\%$ ), followed by  $\gamma$ -terpinene ( $15.1 \pm 0.2\%$ ),  $\beta$ -pinene ( $13.4 \pm 0.1\%$ ), and  $\alpha$ -pinene ( $2.3 \pm 0.5\%$ ). The isomers neral and geranial (aldehydes) were identified as the main oxygenated compounds, comprising  $2.0 \pm 0.2\%$  and  $4.2 \pm 0.4\%$  of the EO, respectively. The remaining composition ( $\sim 1.6\%$ ) was a mixture of decanal (aldehyde), linalool,  $\alpha$ -terpineol, nerol, and geraniol (alcohols) and geranyl acetate (ester). The chemical profile obtained in this study is in accordance with that reported by Franceschi et al. [32] and Koshima et al. [2], where limonene,  $\gamma$ -terpinene, and  $\beta$ -pinene were described as the major components of the terpene fraction, while neral and geranial (citral) were found to be the primary components in the oxygenated fraction [33].

#### IV.3.2. Experimental and predicted data from liquid–liquid equilibrium

For the composition of the phases from the LLE at  $T = (298.2 \pm 0.1)$  K, the components identified in the systems were classified into groups, such as terpenes (1), oxygenated compounds (2), ethanol (3), and water (4). The experimental compositions of the overall, raffinate, and extract phases are represented in mass percentages of the components ( $\% w_i$ ) in Table 3. Except for the system where solvent with 20% water was used, the upper phases were rich in terpenes (raffinate phase) and the bottom phases were rich in solvent (extract phase), as shown in Table 3. From 20 to 30% solvent, inversion of the phases occurred, which may possibly be due to the increase of the extract phase's density with the increase of the water [34].

The partition coefficients of the terpenes and oxygenated compounds ( $k_1$  and  $k_2$ , respectively) [Eq. (1)] and the solvent selectivity ( $S$ ) [Eq. (2)] are shown in Fig. 1. Although the extract phases were abundant in solvent, with lower values of  $\% w_2$  compared to the raffinate

phases, the  $k_2$  values were higher than the  $k_1$  values. This means that the aroma-active components (oxygenated compounds, mainly citral) were separated from the terpenes in the extract phases. The higher selectivity of the solvents for the oxygenated compounds can be proved by the  $S$  values, which were higher than 1.0 for all solvents (Fig. 1). As reported by several authors and for different systems, an increase of the water content in the solvent leads to a decrease of the  $k_i$  values, inducing less migration of the components from the raffinate to the extract phases. However, it was also proved that the increase of the water improves the selectivity of the solvents for the oxygenated compounds, leading to higher  $S$  values [2,6,34–37], as was also observed in these assays.



**Fig. 1** - Distribution coefficients ( $k_i$ ) and solvent selectivity for the oxygenated compounds ( $S$ ) at  $T = (298.2 \pm 0.1)$  K in relation to the water content in the solvent (% , in mass). Experimental: ■,  $k_{\text{terpenes}}$ ; ●,  $k_{\text{oxygenated}}$ ; ▲,  $S$ . Predicted: - - -, NRTL model.

The predicted values of  $k_1$ ,  $k_2$ , and  $S$  using the NRTL parameters are also illustrated in Fig. 1, where it is possible to observe a good description of the experimental values. The good performance of the prediction process using the binary parameters from Koshima et al. [2] can be proved by the low values of the mean deviations shown in Table 5. The predictive capacity

of the model was improved with the increase of water content, and lower deviations were calculated for the oxygenated compounds and water.

**Table 5:** Mean deviations between experimental and calculated compositions of the systems.

$\%w_{4,S}^a$	$\Delta w^b$	Component	$\Delta w^b$
20%	0.04	Terpenes (1)	0.03
30%	0.02	Oxygenated compounds (2)	0.002
40%	0.01	Ethanol (3)	0.03
50%	0.01	Water (4)	0.007
Global deviation	0.02		0.02

<sup>a</sup> Water mass percentage in the solvent.

<sup>b</sup> Calculated by Eq. (3), given as mass fraction.

### IV.3.3. Headspace concentrations

In descending order, the concentrations of the components in the headspace of the crude EO were as follows: limonene ( $4.2 \pm 0.1 \text{ g}\cdot\text{m}^{-3}$ ),  $\beta$ -pinene ( $2.31 \pm 0.06 \text{ g}\cdot\text{m}^{-3}$ ),  $\alpha$ -pinene ( $1.21 \pm 0.04 \text{ g}\cdot\text{m}^{-3}$ ), and  $\gamma$ -terpinene ( $1.13 \pm 0.07 \text{ g}\cdot\text{m}^{-3}$ ) (Table 2). Despite the low value of the mass percentage of  $\alpha$ -pinene in the liquid mixture ( $2.3 \pm 0.4\%$ ), its  $C_i^v$  value is higher than that of the other components present in higher amounts, such as  $\gamma$ -terpinene ( $15.1 \pm 0.2\%$ ). Geranial and neral, which are described as the main components responsible for the intense lime/lemon odor [8,38–41], were the major oxygenated compounds identified in the vapor phase ( $0.050 \pm 0.002 \text{ g}\cdot\text{m}^{-3}$  and  $0.045 \pm 0.001 \text{ g}\cdot\text{m}^{-3}$ , respectively).

The concentrations of components in the headspaces of both raffinate and extract phases are presented in Table 6. The averages and standard deviations values in Table 6 correspond to the headspaces of the three tie-lines from the Table 3, for each solvent. As can be observed in Table 6, the headspace of the LLE phase were mainly composed of ethanol ( $35.4 - 54.3 \text{ g}\cdot\text{m}^{-3}$ ), followed by limonene ( $4.1 - 8.2 \text{ g}\cdot\text{m}^{-3}$ ),  $\beta$ -pinene ( $1.9 - 3.9 \text{ g}\cdot\text{m}^{-3}$ ),  $\gamma$ -terpinene ( $1.2 - 2.3 \text{ g}\cdot\text{m}^{-3}$ ), and  $\alpha$ -pinene ( $1.2 - 1.8 \text{ g}\cdot\text{m}^{-3}$ ), respectively. The  $C_i^v$  values were similar between both phases in terms of major components, despite their discrepancies in the liquid compositions (Table 2). This can be explained by the polarity of the mixture, which increases with the increment of water. In this way, the components with less affinity to the polar solvent (terpenes) are “pushed out” from the solution to the headspace, leading to higher  $C_i^v$  values [28]. On the other hand, the oxygenated compounds, which present a polar portion in their molecules, tend to migrate less to the vapor phase.

**Table 6:** Experimental vapor concentration ( $C_i^v$ , in  $\text{g}\cdot\text{m}^{-3}$ ) at  $T = 298.2$  K and  $p = 1 \times 10^5$  Pa, and odor intensity ( $\Psi_i$ ) of the components in the raffinate and extract phases.<sup>a</sup>

Component ( <i>i</i> )	Solvent 20% water <sup>b</sup>		Solvent 30% water <sup>b</sup>		Solvent 40% water <sup>b</sup>		Solvent 50% water <sup>b</sup>	
	$C_i^v/\text{g}\cdot\text{m}^{-3}$ <sup>c</sup>	$\Psi_i$	$C_i^v/\text{g}\cdot\text{m}^{-3}$ <sup>c</sup>	$\Psi_i$	$C_i^v/\text{g}\cdot\text{m}^{-3}$ <sup>c</sup>	$\Psi_i$	$C_i^v/\text{g}\cdot\text{m}^{-3}$ <sup>c</sup>	$\Psi_i$
Raffinate phase								
Ethanol	54 ± 4	68 ± 5	52 ± 9	67 ± 1	44 ± 1	60 ± 2	43.9 ± 1	60 ± 1
$\alpha$ -Pinene	1.8 ± 0.1	73 ± 4	1.52 ± 0.02	69 ± 1	1.45 ± 0.04	65 ± 2	1.59 ± 0.04	68 ± 2
$\beta$ -Pinene	3.9 ± 0.4	8.4 ± 0.9	3.05 ± 0.02	7.8 ± 0.1	2.92 ± 0.08	7.6 ± 0.2	3.3 ± 0.2	7.9 ± 0.4
Limonene	8 ± 1	35 ± 4	6.1 ± 0.2	31.2 ± 0.8	5.85 ± 0.2	31 ± 1	6.6 ± 0.4	32 ± 2
$\gamma$ -Terpinene	2.3 ± 0.3	12 ± 1	1.72 ± 0.05	10.7 ± 0.3	1.62 ± 0.06	10.4 ± 0.4	1.85 ± 0.08	10.9 ± 0.5
Decanal	0.001 ± 0.001	2.19 ± 0.01	0.001 ± 0.001	2.0 ± 0.3	0.001 ± 0.001	2.41 ± 0.01	0.001 ± 0.001	2.8 ± 0.1
Linalool	0.001 ± 0.001	4 ± 1	0.001 ± 0.001	4.0 ± 0.8	0.002 ± 0.001	4.7 ± 0.5	0.003 ± 0.001	5.8 ± 0.1
Neral	0.02 ± 0.01	8 ± 4	0.025 ± 0.002	8.8 ± 0.8	0.030 ± 0.002	9.3 ± 0.6	0.050 ± 0.002	11.0 ± 0.4
$\alpha$ -Terpineol			0.001 ± 0.001	1.7 ± 0.1	0.001 ± 0.001	1.9 ± 0.3	0.002 ± 0.001	2.5 ± 0.3
Geranial	0.02 ± 0.01	8 ± 4	0.030 ± 0.003	8 ± 1	0.032 ± 0.002	8.9 ± 0.5	0.057 ± 0.005	10.6 ± 0.8
Geranyl Acetate								
Geraniol							0.002 ± 0.001	7 ± 1
Nerol							0.001 ± 0.001	2.5 ± 0.4
Extract Phase								
Ethanol	47.3 ± 0.9	63 ± 1	47.4 ± 0.6	63.0 ± 0.7	44.0 ± 0.7	60.4 ± 0.9	35 ± 2	53 ± 2
$\alpha$ -Pinene	1.37 ± 0.03	63 ± 1	1.34 ± 0.02	62.7 ± 0.9	1.18 ± 0.03	59 ± 2	0.91 ± 0.02	52 ± 1
$\beta$ -Pinene	2.9 ± 0.2	7.6 ± 0.5	2.7 ± 0.1	7.5 ± 0.3	2.47 ± 0.05	7.2 ± 0.1	1.9 ± 0.1	6.6 ± 0.3
Limonene	5.9 ± 0.4	31 ± 2	5.6 ± 0.4	30 ± 2	5.2 ± 0.1	29.3 ± 0.5	4.1 ± 0.3	27 ± 2
$\gamma$ -Terpinene	1.6 ± 0.1	10.5 ± 0.7	1.6 ± 0.1	10.3 ± 0.6	1.47 ± 0.03	10.1 ± 0.2	1.2 ± 0.1	9.3 ± 0.7
Decanal								
Linalool							0.001 ± 0.001	4.7 ± 0.5
Neral	0.017 ± 0.007	8 ± 3	0.012 ± 0.006	7 ± 4	0.017 ± 0.005	8 ± 2	0.032 ± 0.005	10 ± 1
$\alpha$ -Terpineol								
Geranial	0.02 ± 0.01	8 ± 5	0.011 ± 0.002	6 ± 1	0.016 ± 0.005	7 ± 2	0.037 ± 0.006	9 ± 1
Geranyl Acetate								
Geraniol								
Nerol								

<sup>a</sup> Standard uncertainties  $u$  are  $u(T) = 0.1$  K,  $u(p) = 1 \times 10^3$  Pa,  $u(C_i^v)$  is presented after each vapor concentration mean value, and  $u(\Psi_i)$  after the odor intensity value;

<sup>b</sup> Water content in the solvent, given as mass percentages;

<sup>c</sup> The vapor concentration values were obtained by averaging the results from all three tie-lines from the Table 3, for each solvent.

#### IV.3.4. Odor intensity of the components

The experimental odor intensity of the components ( $\Psi_i$ ) identified in the crude acid lime EO is presented in Table 2, where it is possible to observe that  $\alpha$ -pinene is the dominant odor ( $60 \pm 1$ ), followed by limonene ( $27.1 \pm 0.3$ ), neral ( $10.6 \pm 0.1$ ) and geranial ( $10.2 \pm 0.1$ ),  $\gamma$ -terpinene ( $9.2 \pm 0.2$ ),  $\beta$ -pinene ( $7.0 \pm 0.1$ ) and geraniol ( $7.0 \pm 0.2$ ), linalool ( $5.8 \pm 0.1$ ), decanal ( $3.1 \pm 0.1$ ), and  $\alpha$ -terpineol ( $2.84 \pm 0.04$ ), respectively. As mentioned before, the aroma of the citrus EO has been attributed to oxygenated compounds, which are, interestingly, the group present in minor fractions in the liquid EO [2,4,6,16,34–37]. For the example of geraniol, we can observe that even in lower content in the crude EO ( $0.27 \pm 0.01\%$ ) it presents an odor intensity similar to that of  $\beta$ -pinene, which is one of the major compounds identified in the acid lime EO ( $13.4 \pm 0.1\%$ ). This is possibly a consequence of the low geraniol  $ODT$  value ( $7.10 \times 10^{-7} \text{ g} \cdot \text{m}^{-3}$ ) in relation to the  $\beta$ -pinene one ( $8.75 \times 10^{-3} \text{ g} \cdot \text{m}^{-3}$ ) (Table 2).

In the case of the phases from the LLE (Table 6),  $\alpha$ -pinene dominated the odor space of the raffinate phases, while in the extract phases the  $\Psi$  of ethanol had an  $\Psi$  equivalent or higher than the  $\Psi$  of  $\alpha$ -pinene, depending on the solvent used. It should be mentioned that ethanol dominated the odor space of some phases due to its high concentration values in the headspace (Table 6), which is probably a result of its high values of vapor pressure ( $P_{ethanol}^v = 7901 \text{ Pa}$ ) and power law exponent ( $n_{ethanol} = 0.58$ ) (Table 2). In general, the phases exhibited a similar odor profile to the crude EO, in terms of  $\Psi_i$ , independently of the solvent used. Based on these results, we can infer that the proposed approach improves the stability of the acid lime EO by reducing the terpenes content while simultaneously maintaining its original aroma. This behavior can be better observed using the PR tool [19].

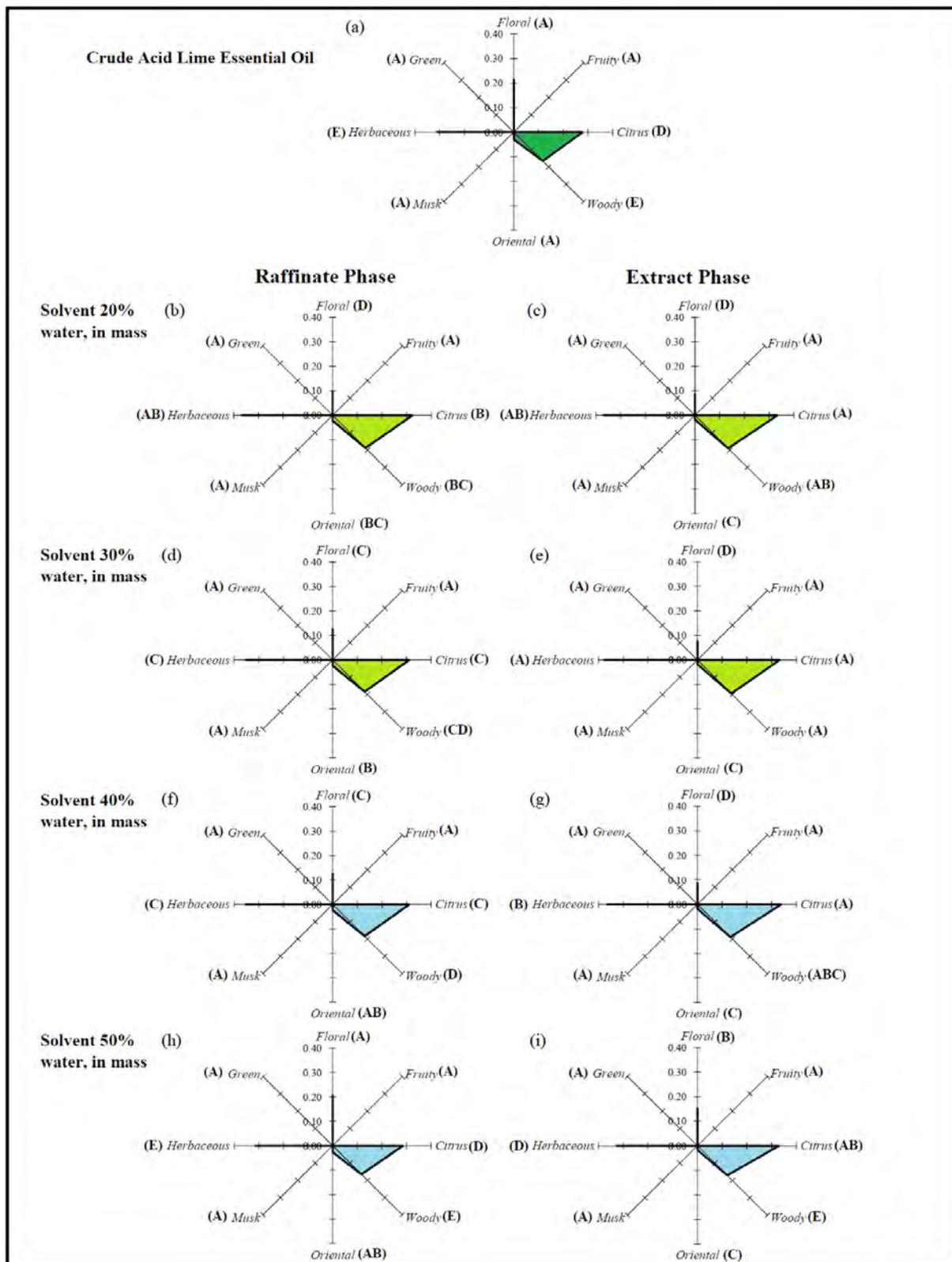
#### IV.3.5. Classification into olfactory families

The experimental odor intensity of each component identified in the vapor samples ( $\Psi_i$ ) was classified into olfactory families as described in Table 2 using Eq. (9). Figure 2 displays the experimental PR for the crude acid lime EO (Fig 2a) and for the phases from LLE (Fig. 2b–i). The crude acid lime EO was classified as primarily herbaceous (31%) with slightly less citrus (28%) and floral (21%), woody (17%), and oriental (3%) nuances. The intense herbaceous scent is mainly attributed to the presence of  $\alpha$ -pinene, which, despite its low mass composition in the liquid mixture ( $2.3 \pm 0.5\%$ ), presents the strongest  $\Psi$  (Table 2), which is a consequence of its

high vapor pressure (633.3 Pa) and power law exponent (0.49). The citrus scent is mainly related to the high concentration of limonene in the headspace ( $4.2 \pm 0.1 \text{ g} \cdot \text{m}^{-3}$ , Table 2).

Analyzing the PRs shown in Fig. 2, no major differences were found among the phases and crude EO. These results proved that the extraction technique allowed the partial removal of compounds responsible for the instability of the crude EO (terpenes) without compromising its typical aroma. From the statistical analysis results, in general, the phases exhibited attenuated herbaceous, citrus, and woody scents in relation to the crude EO, while the extract phases were more herbaceous and citrus than the raffinate phases. This is a consequence of the high mass percentage values of water in the extract phases (Table 3), which induces migration of the terpenes to the vapor phase, contributing more to the final aroma of the mixture. Except for the phases using solvent 50% (Figs. 2h and i), all the phases presented a lower floral scent, which can be explained based on the headspace concentrations in which some oxygenated compounds, responsible for the floral scent, were not identified, mainly in the extract phases (Table 6). Conversely, the use of 50% solvent induced an enhancement in the floral scent due to the presence of other oxygenated compounds in the headspace, such as nerol, geraniol, and linalool (Table 6).

An interesting finding was that although the extract phases have a composition quite different from those of the crude EO and raffinate phases, overall they revealed similar aroma profiles. This is particularly advantageous in terms of industrial applications, once we can obtain extracts with aroma similar to the crude EO, enriched in oxygenated compounds and poor in terpenes, which are associated with instability problems and sensory quality losses. In addition, these extracts are highly soluble in aqueous solutions, facilitating their application in aqueous products, such as beverages and perfumes [42]. According to the aforementioned information, the extract phases using 50% solvent were found to be the best ones obtained from the solvent extraction procedure, since no large differences from the aroma profile of the crude acid lime EO were observed.



**Fig. 2** – Perfumery Radars: (a) crude acid lime essential oil; LLE phases: (b), (d), (f), and (h), raffinate phases; (c), (e), (g), and (i), extract phase. Water content in the solvent by mass percentage: (b) and (c), 20%; (d) and (e), 30%; (f) and (g), 40%; (h) and (i), 50%.

#### IV.4. Conclusions

This work proposed the solvent extraction technique to separate aroma-active compounds from the unstable components in the crude acid lime EO. The key findings were that (i) monoterpenes (limonene,  $\gamma$ -terpinene,  $\beta$ -pinene, and  $\alpha$ -pinene) were the major group of components identified in the crude EO ( $92.2 \pm 0.3\%$ ) and in the raffinate phases (84.9–91.0%), while ethanol was more abundant in the extract phases (47.2–69.3%); (ii) the predicted compositions of the LLE phases exhibited satisfactory results when compared to the experimental data; (iii) the aroma of the crude acid lime EO and the phases from the LLE are dominated by  $\alpha$ -pinene; (iv) components at low mass compositions in the crude EO, like the case of  $\alpha$ -pinene ( $2.3 \pm 0.5\%$ ), can be strongly perceived, possibly due to their low *ODT* and high *n* and  $P_i^v$  values; (v) although the water content in the solvent affected the distribution of the components between the liquid phases, its variation did not strongly affect the aroma profile of the phases; (vi) the PRs of the crude EO and the phases from the LLE presented similar profiles, being classified as herbaceous and citrus scent with floral > woody > oriental nuances. Based on this study, it is possible to infer that ethanol/water mixtures applied for the fractionation of crude acid lime EO were able to generate extract phases enriched in aroma-active components and poor in terpenes with an odor profile similar to that of the crude EO. The extract phases are highly soluble in aqueous solutions, which are more often required for application in aqueous products as aroma ingredients. Among them, the one using 50% solvent seems to be the most promising candidate for this purpose. Therefore, these extracts will increase the solution stability and offer low solvent costs due to the high water content present in the solvent.

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## CHAPTER V: Acid lime essential oil fractionation by solvent extraction: liquid–liquid equilibrium data and operation using continuous equipment

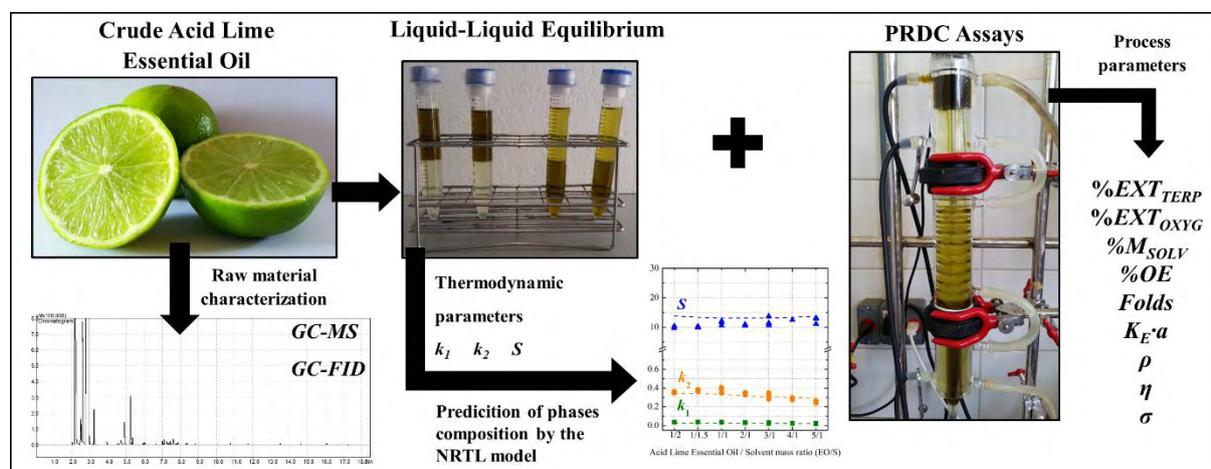
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### V. Graphical abstract



### V. Highlights

- Acid lime essential oil was fractionated using ethanol/water mixtures as solvents.
- Experimental liquid–liquid equilibrium data were obtained.
- Phases composition predicted by the NRTL model exhibited satisfactory results.
- The acid lime essential oil was fractionated using continuous equipment (PRDC).
- 6-fold and 8-fold were obtained using ethanol with 40% and 50% water, respectively.

## V. Abstract

This study focused on the fractionation of *Citrus latifolia* essential oil, which is an important commodity in the international market. New liquid–liquid equilibrium (LLE) data for systems composed of crude acid lime essential oil (CALEO), ethanol, and water at  $298.2 \pm 0.1$  K are presented using different water contents in the solvent and several mass ratios of the CALEO and solvent (EO/S). The performance of the NRTL parameters available in the literature was evaluated by comparing the predicted compositions of the LLE phases with experimental data. In general, a higher water content in the solvent led to less migration of the components from the raffinate into the extract phase but increased the solvent selectivity for oxygenated compounds. Higher EO/S values also caused less migration of the components. The predicted compositions exhibited satisfactory results, with global deviations up to 0.02 in the mass fraction. The CALEO was also fractionated using continuous equipment, namely, a perforated rotating disc contactor (PRDC), with ethanol/water mixtures as solvents at  $298.2 \pm 0.1$  K. The process performance was evaluated by the calculation of extraction indices and by the experimental determination of the physical properties of the output streams (extract and raffinate). As in the LLE, additional water in the solvent led to less extraction of the components and less migration of solvent to the raffinate phase, but higher folds were achieved (i.e., 6-fold using ethanol with 40% (w/w) water as solvent and 8-fold using 50% (w/w) water). Greater water content in the solvent was also related to higher values of density, viscosity and surface tension, especially for the extract phases.

Keywords: Citral, *Citrus latifolia*, Ethanol, NRTL, Perforated rotating disc contactor, Extraction column

## V.1. Introduction

Essential oils (EOs) and terpenic by-products are important commodities in the international market. In 2015, Brazil was ranked as one of the main exporters of these raw materials, with approximately 56 thousand tons exported [1], which corresponds to approximately 8.6% of the world's exports [2]. The high production of citrus EOs drives these numbers, as Brazil is the main exporter of orange EO (approximately 35% of world's exports) [2]. Brazil was the 13<sup>th</sup> main exporter (1.8%) of lemon EOs [1,2] but is ranked as one of the main producers of limes, together with Mexico [3]. No current data were found about acid lime EO, possibly because this raw material is included in the lemon EO classification.

*Citrus latifolia* Tanaka, commonly known as Tahiti, Persian, Bears lime [4], and several other names, is a complex mixture of lemon varieties commonly cultivated in temperate climate, which are generally used as a flavoring food additive and as a beverage base [5]. In Brazil, *C. latifolia* is recognized as acid lime, or “common lemon”, since it is the typical lemon cultivated in the country, mainly in the state of Sao Paulo, being the 5<sup>th</sup> most-common fruit exported [6]. The EO extracted from the acid lime peels, predominantly by cold pressing, is a by-product of the juice industry but is a key ingredient for soft drink formulations, especially for “cola” flavor [7,8]. The acid lime EO is also reported as a constituent in ice creams, candies and baked goods and is used to cover up disagreeable odors in drugs and cosmetic products [9]. As a typical citrus EO, the crude acid lime essential oil (CALEO) is a complex mixture of volatile components [85 – 99% (w/w)], mainly terpene hydrocarbons and their oxygenated derivatives, and non-volatile compounds [1 – 15% (w/w)], such as waxes, pigments, fatty acids, and carotenoids [10]. The volatile portion is mostly composed of limonene (40 – 60%),  $\gamma$ -terpinene (10 – 20%),  $\beta$ -pinene (10 – 16%),  $\alpha$ -pinene (1 – 3%), neral (1 – 5%), and geranial (1 – 6%) (w/w) [7,11–14]. Its composition depends on several factors, such as weather, soil conditions, fruit variety, procedure used for the EO extraction, and others [15]. The terpene fraction is reported to be less stable and more susceptible to degradation when exposed to the air, light or heat, which may generate off-flavor compounds [9,11,15–18]. Moreover, their contribution to the EO aroma is low [15,16]. On the other hand, the oxygenated derivatives, such as citral, composed of a mixture of two geometrical isomers, neral and geranial, are related to the typical lemon aroma, higher stability and acceptability [7,16,19–21]. Thus, the separation of terpenes from oxygenated compounds is a common industrial process aimed at isolating the oxygenated compounds by reducing the amount of terpenes in the EO [15] (a procedure known as deterpenation or folding [11]).

Recent studies have shown that the separation between terpenes and oxygenated compounds in citrus EOs is technically possible using ethanol/water mixtures as the solvent [18,22,23]. Koshima et al. [9] reported liquid–liquid equilibrium data for lemon/lime model systems, composed of limonene,  $\beta$ -pinene,  $\gamma$ -terpinene, citral (the main volatile components present in the EO), ethanol, and water, at  $298.2 \pm 0.1$  K, and also reported adjusted interaction parameters of NRTL and UNIQUAC thermodynamic models. Gonçalves et al. [24] Gonçalves determined LLE data of systems composed of CALEO, ethanol and water, at  $298.2 \pm 0.1$  K, using ethanol with 20, 30, 40, and 50% (w/w) water as solvents. Additionally, the binary parameters of the NRTL model adjusted by Koshima et al. [9] accurately predicted the LLE phases composition obtained by Gonçalves et al. [24]. Both studies developed by Koshima et al. [9] and Gonçalves et al. [24] evaluated the fractionation process with thermodynamic approaches, dealing with parameters such as the partition coefficients of terpenic and oxygenated compounds, as well as solvent selectivity.

The current study proposes an extension of the CALEO deterpenation process by solvent extraction. Additional LLE data of systems composed of CALEO, ethanol, and water, at  $298.2 \pm 0.1$  K were determined, using several concentrations of water in the solvent and different mass proportions of EO and solvent. The performance of the NRTL binary parameters adjusted by Koshima et al. [9] were also evaluated. These predicted compositions were compared to the LLE experimental data. Furthermore, CALEO was submitted to the fractionation process using a perforated rotating disc contactor (PRDC), the same equipment used by Gonçalves et al. [22] for the fractionation of citrus EO model mixtures and crude orange essential oil (COEO). The results obtained for the CALEO were compared to the ones obtained for the COEO [22].

## **V.2. Materials and Experimental procedure**

### **V.2.1. Chemicals**

Crude acid lime essential oil (CALEO) was industrially extracted by cold pressing *Citrus latifolia* peels that were kindly donated by the Louis Dreyfus Company. Solvents were prepared by diluting absolute ethanol (99.99% mass purity, Merck, Germany) with deionized water (Millipore, Milli-Q, Bedford, USA). The water mass percentages in the solvents were:  $20 \pm 1\%$ ,  $24.4 \pm 0.3\%$ ,  $31.4 \pm 0.7\%$ ,  $42.6 \pm 0.5\%$  and  $51 \pm 1\%$  for the determination of LLE data, and  $40.4 \pm 0.3\%$  and  $51.2 \pm 0.5\%$  for the fractionation process trials in continuous equipment. The CAS numbers, experimental purities, source and experimental physical properties (density,

dynamic viscosity and surface tension) of the main components present in the systems and mixtures used in the assays are shown in Table 1.

## V.2.2. Experimental procedure

### V.2.2.1. Chemical analysis

#### V.2.2.1.1. Characterization of the chemical compounds and mixtures

Purities and retention times of the chromatographic-grade components  $\beta$ -pinene, limonene,  $\gamma$ -terpinene, citral and ethanol were assessed by gas chromatography, without further purification. The analysis was performed in a gas chromatograph with a flame ionization detector (GC-FID, Shimadzu GC 2010 AF, Japan) and an automatic injector (Shimadzu AOC 20i, Japan) using a nitroterephthalic acid-modified polyethylene glycol (DB-FFAP) capillary column (0.25  $\mu\text{m}$ , 30 m  $\times$  0.25 mm i.d.; Agilent, USA). Experimental conditions and procedures were the same as those used by Gonçalves et al. [22]: helium ( $\geq 99.99\%$ , Linde, Brazil) as the carrier gas at 1.13  $\text{mL}\cdot\text{min}^{-1}$ , sample injection (1.0  $\mu\text{L}$ ) with 1/50 split ratio at 523.2 K, detector (FID) temperature of 553.2 K, column temperature program of 373.2 – 513.2 K at 8  $\text{K}\cdot\text{min}^{-1}$  and held at 513.2 K for 1 min (running time of 18.5 min). Samples were diluted in 1-propanol (99.9%, Sigma-Aldrich, EUA) with a 1/1 mass ratio before injection. The water content in the samples was determined by Karl Fischer titration (Metrohm 787 KF Titrino, Switzerland) using the Karl Fischer reagent (CombiTitrant 5 mg  $\text{H}_2\text{O}\cdot\text{mL}^{-1}$ , Merck, Germany).

Experimental densities ( $\rho$ , in  $\text{kg}\cdot\text{m}^{-3}$ ) and dynamic viscosities ( $\eta$ , in  $\text{mPa}\cdot\text{s}$ ) were measured in a bench digital densimeter (Anton Paar DMA 4500, Austria) and in a falling-ball automated micro viscometer (Anton Paar AMVn, Austria), respectively, according to the procedure adopted by Gonçalves et al. [25]. Surface tensions ( $\sigma$ , in  $\text{mN}\cdot\text{m}^{-1}$ ) were determined by a force tensiometer (Attension Sigma 702, Finland) as conducted by Gonçalves et al. [22]. All measurements were performed at least in triplicate, with experimental uncertainties of  $\leq 0.01 \text{ kg}\cdot\text{m}^{-3}$  for density,  $\leq 0.03 \text{ mPa}\cdot\text{s}$  for dynamic viscosity and  $\leq 0.1 \text{ mN}\cdot\text{m}^{-1}$  for surface tension.

**Table 1:** CAS numbers, supplier and experimental purities, source and experimental physical properties at  $T = 298.2$  K.<sup>a</sup>

Material	CAS registry number	Supplier Purity (%)	Experimental Purity (%) <sup>b</sup>	Source	$\rho$ (kg·m <sup>-3</sup> ) <sup>c</sup>	$\eta$ (mPa·s) <sup>d</sup>	$\sigma$ (mN·m <sup>-1</sup> ) <sup>e</sup>
<i>Standards</i>							
(-)- $\beta$ -Pinene	18172-67-3	99.00	99.87	Sigma-Aldrich, USA	866.95	1.53	27.4
(R)-(+)-Limonene	5989-27-5	98.80	98.81	Sigma-Aldrich, USA	841.35*	0.92*	27.6*
$\gamma$ -Terpinene	99-85-4	97.00	97.69	Sigma-Aldrich, USA	845.16	0.85	27.3
Citral	5392-40-5	95.00	99.05	Sigma-Aldrich, USA	884.84	1.93	31.9
Ethanol	64-17-5	99.80	99.99	Merck, Germany	785.18*	1.06*	21.6*
Water	7732-18-5				997.04*	0.87*	71.1*
<i>Solvents (mass percentage of water in ethanol)</i>							
20 $\pm$ 1%					841.91	1.68	24.8
24.4 $\pm$ 0.3%					852.24	1.73	25.1
31.4 $\pm$ 0.7%					865.50*	1.80*	25.6*
42.6 $\pm$ 0.5%					890.10*	2.18*	26.7*
51 $\pm$ 1%					909.35	2.24	28.2
Crude Acid Lime				Louis Dreyfus			
Essential Oil (CALEO)				Company, Brazil	864.57	1.23	25.3

<sup>a</sup> Standard uncertainties  $u$  are  $u(T) = 0.1$  K,  $u(\rho) = 0.01$ ,  $u(\eta) \leq 0.03$  and  $u(\sigma) \leq 0.1$ ;

<sup>b</sup> Experimentally determined by GC-FID, given as mass percentage, without further purification;

<sup>c</sup> Density;

<sup>d</sup> Dynamic viscosity;

<sup>e</sup> Surface tension;

\* Experimental data in agreement with values previously reported in the literature [18,22,25].

### V.2.2.1.2. Chemical characterization of the crude acid lime essential oil

The volatile fraction of CALEO was characterized using a gas chromatograph coupled to a mass spectrometer (GC-MS, Shimadzu QP 2010 Plus, Japan). The mass spectra of the components found in CALEO were compared to those contained in the Solutions CG-MS software (version 2.5), based on the NIST 08 and NIST 08s mass spectra database. For accurate and reliable identification, some components were also identified by comparison with the retention times of standards injected under the same conditions as the sample. The conditions used in the CG-MS analysis were the same used for CG-FID by Gonçalves et al. [18], with the column interface at 518.2 K, ion source at 473.2 K, mass spectral scanning range from  $m/z$  40 to  $m/z$  800 and 70 eV ion source energy. Then, the composition of CALEO was evaluated by internal normalization in GC-FID, where compounds with mass percentages lower than 0.1% were ignored. Table 2 displays the chemical composition of CALEO (volatile fraction), with compounds grouped into terpenes and oxygenated compounds.

The Kovats retention index of each component ( $KI_i$ ) was calculated by Eq. (1). For that, the alkane standard  $C_{10}$ - $C_{40}$  (Sigma-Aldrich, USA) was analyzed under the same GC-MS conditions.

$$KI_i = 100 \times C_{i-1} + 100 \times \left[ \frac{\log RT_i - \log RT_{i-1}}{\log RT_{i+1} - \log RT_{i-1}} \right] \quad (1)$$

where  $C_{i-1}$  is the number of carbons in the alkane immediately preceding the analyte,  $RT_i$  is the analyte retention time,  $RT_{i-1}$  is the retention time of the alkane immediately preceding the analyte, and  $RT_{i+1}$  is the retention time of the alkane immediately after the analyte.

The measurements were performed in triplicate for the CALEO. Type A standard uncertainty [26] in the mass fractions was estimated to be less than or equal to 0.001 [or 0.1% ( $w/w$ )].

**Table 2:** Chemical characterization of crude acid lime essential oil (CALEO), retention time, identification procedure, Kovats Index ( $KI_i$ ), molar mass, and mass percentage of each identified component (%w).

Component Group	Retention Time (min)	Identification <sup>a</sup>	$KI_i^b$	Molar mass (g·mol <sup>-1</sup> )	%w <sub>i</sub> <sup>c</sup>
<b>Terpenes</b>				<b>137.7<sup>d</sup></b>	<b>95.6</b>
$\alpha$ -Pinene	2.21	Standard/ $KI^*$	1461	136.2	2.7
$\beta$ -Pinene	2.47	Standard/ $KI^*$	1479	136.3	13.1
Myrcene	2.55	NIST-MS	1485	136.3	1.4
<i>d</i> -Limonene	2.84	Standard/ $KI^*$	1604	136.3	60.0
$\gamma$ -Terpinene	3.02	Standard	1617	136.3	14.6
<i>p</i> -Cymene	3.13	Standard/ $KI^*$	1624	134.2	0.1
Terpinolene	3.19	NIST-MS	1628	136.2	0.7
$\delta$ -Elemene	4.58	NIST-MS	1802	204.4	0.1
$\beta$ -Caryophyllene	5.76	NIST-MS/ $KI^*$	1860	204.4	1.2
$\beta$ -Elemene	6.01	NIST-MS	1871	204.4	0.5
$\alpha$ -Bergamotene	6.56	NIST-MS	1894	204.4	0.1
$\beta$ -Farnesene	6.82	NIST-MS/ $KI^*$	1904	204.4	0.1
$\beta$ -Bisabolene	7.39	NIST-MS/ $KI^*$	2034	204.4	1.0
$\beta$ -Germacrene	7.89	NIST-MS	2057	204.4	0.1
<b>Oxygenated Compounds</b>				<b>155.8<sup>d</sup></b>	<b>4.4</b>
Decanal	4.83	Standard	1815	156.3	0.1
Linalool	5.18	Standard/ $KI^*$	1833	154.2	0.2
Neral	6.95	Standard/ $KI^*$	2012	152.2	1.1
$\alpha$ -Terpineol	7.02	Standard/ $KI^*$	2015	154.2	0.2
Geranial	7.56	Standard/ $KI^*$	2042	152.2	2.3
Geranyl Acetate	7.69	NIST-MS/ $KI^*$	2047	196.3	0.2
Geraniol	8.22	Standard/ $KI^*$	2070	154.3	0.2
Bisabolol	8.73	NIST-MS	2092	222.4	0.1

<sup>a</sup> Identified by GC-MS (NIST-MS library), and by comparison with the standard retention time and/or with  $KI$  values from the literature;

<sup>b</sup> Kovats Index, calculated by Eq. (1);

<sup>c</sup> Quantified by GC-FID internal normalization, the standard uncertainty  $u$  is  $u(w) = 0.1\%$ ;

<sup>e</sup> Average molar mass of the group (terpenes or oxygenated compounds).

\* Kovats Index in agreement with value previously reported in the literature [18,23].

## V.2.2.2. Liquid–liquid equilibrium (LLE)

### V.2.2.2.1. LLE determination

The procedure for determination of LLE experimental data was the same as used in previous assays [18,25]. For the construction of the systems, CALEO was contacted with the solvent [ethanol with 20%, 24%, 30%, 40%, or 50% (w/w) water] in a polypropylene tube (Corning, USA) using several mass ratios between the EO and the solvent (EO/S = 1/2, 1,1.5, 1/1, 1.5/1, 2/1, 3/1, 4/1, and 5/1, depending on the solvent). After to the suitable contact between the liquids, the tubes were centrifuged (Thermo Electron Corporation CR3i, France) at 5000 g for 30 min at  $298.2 \pm 0.1$  K and maintained in a thermostatic bath (Marconi MA-184, Brazil) with

controlled temperature of  $298.2 \pm 0.1$  K for 20 h. After that, the two homogeneous and clear phases, the terpene-rich and solvent-rich phases, were separately collected by syringes and submitted to GC-FID analysis to quantify the terpenes, oxygenated compounds, and ethanol, while the water was quantified by Karl Fischer titration. The conditions for the GC-FID analyses were described in section 2.2.1.1.

Ethanol, terpenes and oxygenated compounds were identified in the phases by comparing their retention times with the ones of pure compounds (Table 2) and quantified using the external standard method. The measurements were performed in duplicate for each phase, and Type A standard uncertainty [26] was estimated to be less than or equal to 0.1% (w/w). By convention, the terpene-rich phases were called “raffinate phases”, while the solvent-rich phases were called “extract phases”. Terpenes and oxygenated compounds were grouped separately; therefore, the LLE data were represented as terpenes (1), oxygenated compounds (2), ethanol (3) and water (4).

#### **V.2.2.2.2. Experimental data validation**

The validity of the LLE data was evaluated by the procedure proposed by Marcilla et al. [26], where the least-squares fitting procedure was applied to calculate the masses of the phases from the LLE using their experimental compositions. The deviation ( $\delta$ , in %) between the calculated masses and the overall composition mass was calculated by Eq. (2).

$$\delta = \left( \frac{(M_{RP} + M_{EP}) - M_{OC}}{M_{OC}} \right) \times 100 \quad (2)$$

where  $M_{RP}$  and  $M_{EP}$  are the calculated masses of the raffinate and extract phases, respectively, and  $M_{OC}$  is the experimental mass of the initial mixture (overall composition). According to Marcilla et al. [26],  $\delta \leq 0.5\%$  represents satisfactory LLE data, meaning that tie-lines with  $\delta > 0.5\%$  were rejected.

#### **V.2.2.2.3. Prediction of the phases' compositions using parameters from the literature**

The binary interaction parameters of the NRTL model [27] adjusted by Koshima et al. [9] for the lemon/lime EO model systems composed of  $\beta$ -pinene, limonene,  $\gamma$ -terpinene, citral, ethanol, and water, were used to predict the compositions of the LLE phases of systems composed of CALEO and solvent, at  $298.2 \pm 0.1$  K. Several LLE data were experimentally determined in this study to evaluate the capacity of the NRTL parameters to predict the phase compositions from different overall compositions and different water content in the solvents.

As mentioned above, the CALEO was expressed as a mixture of two groups of components, terpenes (1) and oxygenated compounds (2), whose average molar masses are indicated in Table 2. For the prediction procedure, limonene's parameters were used for the calculation of the mass fractions of terpenes, while the parameters of citral were used for the oxygenated compounds. This approach has been efficiently used in previous works [18,24].

The procedure for predicting phase compositions involves flash calculations from the OC of the experimental tie lines (Table 3), as proposed by Stragevitch and d'Avila [28]. The deviation between the experimental and the calculated compositions in the systems ( $\Delta w$ ) was calculated by Eq. (3).

$$\Delta w = \sqrt{\frac{\sum_{n=1}^N \sum_{i=1}^K \left[ \left( w_{i,n}^{RP,exp} - w_{i,n}^{RP,calc} \right)^2 + \left( w_{i,n}^{EP,exp} - w_{i,n}^{EP,calc} \right)^2 \right]}{2NK}} \quad (3)$$

where  $N$  is the total number of tie lines,  $K$  is the total number of components,  $w$  is the mass fraction of the component  $i$  [terpenes (1), oxygenated compounds (2), ethanol (3), water (4)], the subscript  $n$  is the tie line number, the superscripts  $RP$  and  $EP$  represent the raffinate and extract phases, respectively, and the superscripts  $exp$  and  $calc$  refer to experimental and calculated compositions.

#### V.2.2.2.4. Equilibrium parameters

The LLE data are frequently discussed in terms of the distribution of the components between the raffinate and the extract phases [ $k_i$ , Eq. (4)] and the solvent selectivity for the oxygenated compounds [ $S$ , Eq. (5)]. The predicted  $k_i$  and  $S$  values were compared to the experimental ones to evaluate the performance of the NRTL parameters.

$$k_i = \frac{w_{i,EP}}{w_{i,RP}} \quad (4)$$

$$S = \frac{k_2}{k_1} \quad (5)$$

**Table 3:** Experimental liquid–liquid equilibrium data for systems composed of crude acid lime essential oil (CALEO) and solvent, represented by terpenes (1), oxygenated compounds (2), ethanol (3), and water (4), for mass fractions  $w$  at  $T = 298.2$  K and  $p = 1 \times 10^5$  Pa.<sup>a</sup>

EO/S <sup>b</sup>	Overall Composition (OC)				Raffinate Phase (RP)				Extract Phase (EP)				$\delta^c$
	$w_1$	$w_2$	$w_3$	$w_4$	$w_1$	$w_2$	$w_3$	$w_4$	$w_1$	$w_2$	$w_3$	$w_4$	
Ethanol with $20 \pm 1\%$ (w/w) water													
1/2	0.310	0.024	0.528	0.138	0.880	0.036	0.078	0.006	0.077	0.018	0.711	0.193	0.04
	0.310	0.024	0.529	0.137	0.881	0.036	0.077	0.006	0.075	0.019	0.716	0.190	0.05
	0.310	0.024	0.530	0.137	0.877	0.036	0.081	0.006	0.075	0.019	0.715	0.192	0.01
1/1	0.463	0.035	0.402	0.100	0.852	0.043	0.099	0.006	0.095	0.028	0.688	0.189	0.05
	0.465	0.035	0.401	0.099	0.849	0.044	0.100	0.006	0.090	0.027	0.693	0.190	0.01
	0.465	0.035	0.400	0.100	0.849	0.044	0.100	0.007	0.089	0.027	0.693	0.191	0.02
Ethanol with $24.4 \pm 0.3\%$ (w/w) water													
1/2	0.329	0.025	0.488	0.158	0.878	0.039	0.076	0.006	0.068	0.019	0.683	0.231	0.07
	0.308	0.025	0.504	0.163	0.859	0.038	0.093	0.010	0.057	0.018	0.692	0.233	0.01
	0.317	0.025	0.498	0.161	0.894	0.039	0.060	0.007	0.063	0.019	0.690	0.228	0.01
1/1	0.463	0.037	0.377	0.123	0.878	0.050	0.064	0.008	0.052	0.024	0.687	0.238	0.01
	0.463	0.037	0.377	0.123	0.878	0.050	0.066	0.006	0.058	0.024	0.678	0.240	0.10
	0.463	0.037	0.377	0.123	0.869	0.050	0.073	0.008	0.055	0.024	0.682	0.238	0.01
Ethanol with $31.4 \pm 0.7\%$ (w/w) water													
1/2	0.311	0.023	0.459	0.207	0.897	0.040	0.059	0.004	0.031	0.014	0.650	0.305	0.03
	0.312	0.023	0.456	0.209	0.900	0.039	0.056	0.004	0.032	0.014	0.645	0.309	0.04
1/1.5	0.464	0.032	0.347	0.157	0.894	0.046	0.056	0.005	0.033	0.017	0.651	0.298	0.41
	0.463	0.033	0.347	0.157	0.894	0.048	0.054	0.005	0.033	0.017	0.647	0.302	0.21
1/1	0.461	0.035	0.347	0.157	0.887	0.050	0.058	0.005	0.032	0.019	0.647	0.302	0.28
	0.468	0.036	0.342	0.154	0.871	0.052	0.073	0.005	0.029	0.018	0.644	0.310	0.25
	0.465	0.035	0.344	0.155	0.883	0.050	0.062	0.005	0.030	0.020	0.640	0.310	0.06
	0.465	0.035	0.345	0.155	0.883	0.050	0.063	0.004	0.030	0.020	0.637	0.313	0.03
	0.465	0.035	0.345	0.155	0.883	0.050	0.063	0.004	0.030	0.020	0.637	0.313	0.03
2/1	0.619	0.047	0.227	0.107	0.870	0.059	0.065	0.006	0.027	0.019	0.610	0.344	0.01
	0.616	0.047	0.233	0.105	0.873	0.059	0.061	0.007	0.028	0.021	0.635	0.316	0.22
	0.617	0.047	0.232	0.104	0.870	0.059	0.066	0.005	0.028	0.020	0.628	0.324	0.20
3/1	0.693	0.054	0.174	0.079	0.874	0.063	0.058	0.004	0.027	0.021	0.614	0.338	0.20
	0.692	0.056	0.173	0.079	0.870	0.065	0.060	0.005	0.026	0.020	0.599	0.355	0.05
	0.695	0.055	0.173	0.077	0.870	0.063	0.062	0.005	0.027	0.022	0.616	0.335	0.24
	0.696	0.053	0.173	0.078	0.875	0.062	0.055	0.007	0.018	0.018	0.619	0.346	0.03
4/1	0.741	0.057	0.140	0.062	0.871	0.064	0.060	0.005	0.019	0.017	0.590	0.374	0.03
	0.742	0.057	0.138	0.062	0.873	0.062	0.059	0.005	0.021	0.018	0.587	0.374	0.17
5/1	0.774	0.059	0.115	0.052	0.873	0.065	0.057	0.005	0.016	0.016	0.565	0.403	0.00

EO/S <sup>b</sup>	Overall Composition (OC)				Raffinate Phase (RP)				Extract Phase (EP)				$\delta^c$
	w <sub>1</sub>	w <sub>2</sub>	w <sub>3</sub>	w <sub>4</sub>	w <sub>1</sub>	w <sub>2</sub>	w <sub>3</sub>	w <sub>4</sub>	w <sub>1</sub>	w <sub>2</sub>	w <sub>3</sub>	w <sub>4</sub>	
	0.774	0.059	0.115	0.052	0.866	0.064	0.064	0.006	0.021	0.017	0.559	0.404	0.11
	0.772	0.059	0.117	0.053	0.870	0.064	0.059	0.006	0.016	0.015	0.565	0.404	0.02
Ethanol with 42.6 ± 0.5% (w/w) water													
1/2	0.312	0.023	0.382	0.283	0.917	0.047	0.032	0.004	0.009	0.011	0.558	0.422	0.03
	0.306	0.026	0.383	0.284	0.913	0.056	0.028	0.003	0.007	0.011	0.563	0.419	0.09
1/1.5	0.310	0.026	0.381	0.283	0.905	0.056	0.035	0.004	0.007	0.011	0.561	0.420	0.06
	0.370	0.028	0.354	0.249	0.897	0.055	0.044	0.004	0.010	0.010	0.561	0.419	0.07
1/1	0.372	0.028	0.350	0.250	0.897	0.054	0.045	0.004	0.010	0.010	0.559	0.420	0.01
	0.467	0.036	0.293	0.205	0.892	0.058	0.046	0.004	0.011	0.011	0.557	0.421	0.01
1.5/1	0.463	0.036	0.288	0.214	0.910	0.060	0.027	0.004	0.011	0.011	0.552	0.426	0.00
	0.458	0.035	0.293	0.213	0.903	0.059	0.034	0.004	0.010	0.012	0.557	0.422	0.01
2/1	0.555	0.042	0.237	0.166	0.888	0.061	0.048	0.004	0.009	0.011	0.549	0.430	0.02
	0.558	0.043	0.229	0.170	0.896	0.061	0.040	0.004	0.010	0.013	0.539	0.438	0.00
3/1	0.532	0.041	0.243	0.183	0.903	0.062	0.031	0.004	0.010	0.013	0.539	0.438	0.04
	0.620	0.047	0.194	0.139	0.886	0.063	0.047	0.004	0.009	0.011	0.535	0.445	0.05
1/1	0.620	0.047	0.193	0.140	0.900	0.063	0.033	0.004	0.009	0.012	0.540	0.439	0.01
	0.621	0.047	0.190	0.141	0.903	0.063	0.029	0.004	0.007	0.013	0.541	0.439	0.03
2/1	0.614	0.047	0.195	0.144	0.902	0.063	0.031	0.004	0.009	0.014	0.519	0.459	0.12
	0.696	0.053	0.149	0.101	0.885	0.065	0.046	0.004	0.007	0.010	0.521	0.461	0.01
3/1	0.693	0.053	0.146	0.109	0.896	0.065	0.035	0.004	0.005	0.012	0.517	0.466	0.02
	0.675	0.051	0.158	0.115	0.885	0.064	0.046	0.005	0.007	0.011	0.520	0.462	0.01
Ethanol with 51 ± 1% (w/w) water													
1/1	0.465	0.035	0.248	0.252	0.900	0.062	0.034	0.004	0.004	0.006	0.476	0.514	0.03
	0.468	0.036	0.246	0.250	0.909	0.064	0.023	0.004	0.004	0.006	0.478	0.511	0.01
2/1	0.467	0.036	0.246	0.251	0.906	0.064	0.027	0.003	0.002	0.006	0.472	0.519	0.01
	0.620	0.047	0.165	0.168	0.899	0.066	0.031	0.004	0.002	0.006	0.458	0.534	0.00
3/1	0.620	0.047	0.161	0.171	0.908	0.067	0.021	0.004	0.003	0.007	0.460	0.530	0.02
	0.614	0.047	0.165	0.175	0.901	0.065	0.030	0.004	0.002	0.006	0.455	0.536	0.01
1/1	0.696	0.053	0.124	0.127	0.903	0.068	0.025	0.004	0.003	0.005	0.457	0.536	0.03
	0.697	0.053	0.121	0.129	0.901	0.067	0.029	0.003	0.002	0.005	0.437	0.557	0.02

<sup>a</sup> Standard uncertainties  $u$  are  $u(w) = 0.001$ ,  $u(T) = 0.1$  K, and  $u(p) = 1 \times 10^3$  Pa.

<sup>b</sup> Nominal mass ratio between the acid lime essential oil and the solvent.

<sup>c</sup> Relative deviation, calculated by Eq. (2), in %.

### V.2.2.3. Continuous equipment assays

#### V.2.2.3.1. Equipment operation

The CALEO was submitted to the fractionation process using continuous equipment on a laboratory scale. The perforated rotating disc contactor (PRDC) was used for this aim, and the operational procedure was the same as that conducted by Gonçalves et al. [22] for crude orange EO (COEO) fractionation. The PRDC had an extraction region height of 15.5 cm and a volume of 71.43 cm<sup>3</sup> with 10 polypropylene disks, which had 1.62 cm<sup>2</sup> of perforated area (free flow area) and 3.80 cm<sup>2</sup> of non-perforated area. The disc rotation speed was set at 150 rpm, and the solvent/feed mass flow ratio used was 1/1. The extract was the continuous phase, and the raffinate was the dispersed phase. Due to the densities of the liquids, the CALEO (feed) was inserted into the bottom of the PRDC, and the extract phase was collected at the bottom, while the solvent was inserted into and the raffinate was collected from the upper region. Samples of output streams (raffinate and extract phases) were collected at 15, 30, 45, 60, 75 and 105 minutes after the stabilization of the process and were immediately submitted to CG-FID and Karl Fischer analyses, according to methodologies previously described in section 2.2.1.1. Samples from the last collection time (105 minutes) were also submitted to the determination of their physical properties values. All assays were conducted at atmospheric pressure (749 mmHg) and a controlled temperature of 298.2 ± 0.1 K with a thermostatic bath (Marconi MA-184, Brazil) that allowed water flowing through the column jacket (operational details can be found in Gonçalves et al. [22]). To evaluate the fractionation process performance, some indices were calculated as described in following sections.

Mass balances were calculated to check the validity of the experimental results. The overall mass balance provides an overview of the process as inlet and output masses are considered the total mass flow of the streams. The error on the overall mass balance ( $E_{OMB}$ , in %) was determined by Eq. (6), while the relative error of a specific component  $i$  ( $E_{MBi}$ , in %) was calculated by Eq. (7).

$$E_{OMB} = \frac{|(F + S) - (E + R)|}{(F + S)} \times 100 \quad (6)$$

$$E_{MBi} = \frac{|(w_{i,F} \cdot F + w_{i,S} \cdot S) - (w_{i,E} \cdot E + w_{i,R} \cdot R)|}{(w_{i,F} \cdot F + w_{i,S} \cdot S)} \times 100 \quad (7)$$

where  $F$ ,  $S$ ,  $R$  and  $E$  are the feed, solvent, raffinate and extract mass flows, respectively, in  $\text{kg}\cdot\text{s}^{-1}$ , while  $w_{i,F}$ ,  $w_{i,S}$ ,  $w_{i,R}$  and  $w_{i,E}$  are the mass fractions of the component  $i$  in the feed, solvent, raffinate and extract streams, respectively.

### V.2.2.3.2. Evaluation of the process performance

As proposed by Gonçalves et al. [22], some indices were calculated to evaluate the fractionation performance of using the PRDC, such as the percentage of oxygenated compounds and terpenes extracted from the feed [% $EXT_{OXYG}$ , Eq. (8) and % $EXT_{TERP}$ , Eq. (9), respectively], the mass percentage of oxygenated compounds in the extract phase (on a solvent-free basis) [% $OE$ , Eq. (10)], the percentage of solvent migration to the raffinate phase [% $M_{SOLV}$ , Eq. (11)], and the total concentration of the oxygenated compounds in the extract in relation to the terpenes [ $Folds$ , Eq. (13)].

$$\%EXT_{OXYG} = \frac{w_{2,E} \cdot E}{w_{2,F} \cdot F} \times 100 \quad (8)$$

$$\%EXT_{TERP} = \frac{w_{1,E} \cdot E}{w_{1,F} \cdot F} \times 100 \quad (9)$$

$$\%OE = \frac{w'_{2,E} \cdot E}{(w'_{2,E} \cdot E + w'_{1,E} \cdot E)} \times 100 \quad (10)$$

$$\%M_{SOLV} = \frac{w_{3,R} \cdot R + w_{4,R} \cdot R}{w_{3,S} \cdot S + w_{4,S} \cdot S} \times 100 \quad (11)$$

The subscript numbers correspond to terpenes (1), oxygenated compounds (2), ethanol (3) and water (4). The superscript ' relates the composition on a solvent-free basis, calculated by Eq. (12).

$$w'_{i,E} = \frac{w_{i,E}}{(1 - w_{3,E} - w_{4,E})} \quad (12)$$

The ratio of the concentration of the oxygenated compounds in the fractionated CALEO to the concentration in the initial composition (feed composition), industrially known as fold, was calculated by Eq. (13).

$$Folds = \frac{\%OE}{100 \times w_{2,F}} \quad (13)$$

The volumetric overall mass transfer coefficient, which refers to the amount of solute (oxygenated compounds) mass flow that is transferred to the extract phase per unit of extraction volume, was also calculated according to the methodology applied by Gonçalves et al. [22] based on a technique previously proposed by Treybal [29]. The  $K_E \cdot a$  values were based on the solute concentration in the continuous phase (extract) inside the extraction region because the extract phase offers more resistance to solute transference [30]. Additionally, the solute transference from the raffinate phase to the extract phase is dependent on its concentration in both phases, resulting in an inconstant mass transference [22]. The  $K_E \cdot a$  was estimated by Eq. (14).

$$K_E \cdot a = \frac{E \cdot (w_{2,E} - w_{2,S})}{v \cdot \frac{\Delta w_A - \Delta w_B}{\ln\left(\frac{\Delta w_A}{\Delta w_B}\right)}} \quad (14)$$

where  $K_E$  is the overall mass transfer coefficient of oxygenated compounds ( $\text{kg}_{\text{oxyg}} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot (\text{kg}_{\text{oxyg}} \cdot \text{kg}_{\text{extract}}^{-1})^{-1}$ ),  $a$  is the mass transfer area per extraction region volume unit ( $\text{m}^2 \cdot \text{m}^{-3}$ ),  $\Delta w_A$  is the absolute difference between  $w_{2,F}$  and  $w_{2,E}$ , and  $\Delta w_B$  is the absolute difference between  $w_{2,S}$  and  $w_{2,R}$  (expressed as  $w_{2,E}^*$ );  $v$  is the volume of the extraction region ( $71.43 \cdot 10^{-6} \text{ m}^3$ ). Since the solvent is composed of only ethanol and water, the term  $w_{2,S}$  is zero. The term  $w_{2,E}^*$  corresponds to the mass fraction of oxygenated compounds in the extract phase at equilibrium with the raffinate phase ( $w_{2,R}$ ).

For the estimation of  $K_E \cdot a$ , the equilibrium curves for citral, representing the oxygenated compounds, were adjusted for the solvent with 40% (w/w) water from experimental data reported by Koshima et al. [9] [Eq. (15)] and for the 50% (w/w) water solvent from experimental data not reported. [Eq. (16)].

$$w_{2,E}^* = -0.2438 \times w_{2,R}^2 + 0.2300 \times w_{2,R} \quad R^2 = 0.9999 \quad (15)$$

$$w_{2,E}^* = -0.1571 \times w_{2,R}^2 + 0.0882 \times w_{2,R} \quad R^2 = 0.9676 \quad (16)$$

#### V.2.2.3.4. Statistical analysis

Experimental and estimated parameters were compared by variance analysis with Duncan's test [31] at a significance level of  $P \leq 0.05$ , using SAS® software (version 9.2, SAS Institute Inc., USA).

### V.3. Results and Discussion

#### V.3.1. Crude acid lime essential oil characterization

The chemical composition of CALEO, as assessed by GC-FID by internal normalization, is shown in Table 2. Components with a mass percentage (%w) lower than 0.1% were not considered. The chemical analysis revealed that the CALEO is mainly composed of monoterpene hydrocarbons, such as limonene (60.0%),  $\gamma$ -terpinene (14.6%), and  $\beta$ -pinene (13.1%), and a complex mixture of others monoterpenes and sesquiterpenes (7.9%). The remaining 4.4% is a mixture of oxygenated compounds, of which geranial and neral are the main representatives [2.3% and 1.1%, respectively]. The main components identified in CALEO are in concordance with the literature [7,9,12,13,24,32], and some differences in the %w may be related to the EO extraction procedure, cultivated area, fruit quality, etc.

As demonstrated by Koshima et al. [9] and adopted in previous studies [18,24], the terpenes were assumed to have similar chemical behavior in the LLE (equivalent partition coefficients), and for this reason, this group can be represented by the most common terpene in the EO, limonene. Similarly, the oxygenated fraction was represented by citral, which is the main oxygenated compound. This approach was applied for the quantification of the components in the LLE by external standardization and to predict the phases' compositions using the NRTL parameters from the literature [9], with the average molar mass calculated for each group (Table 2).

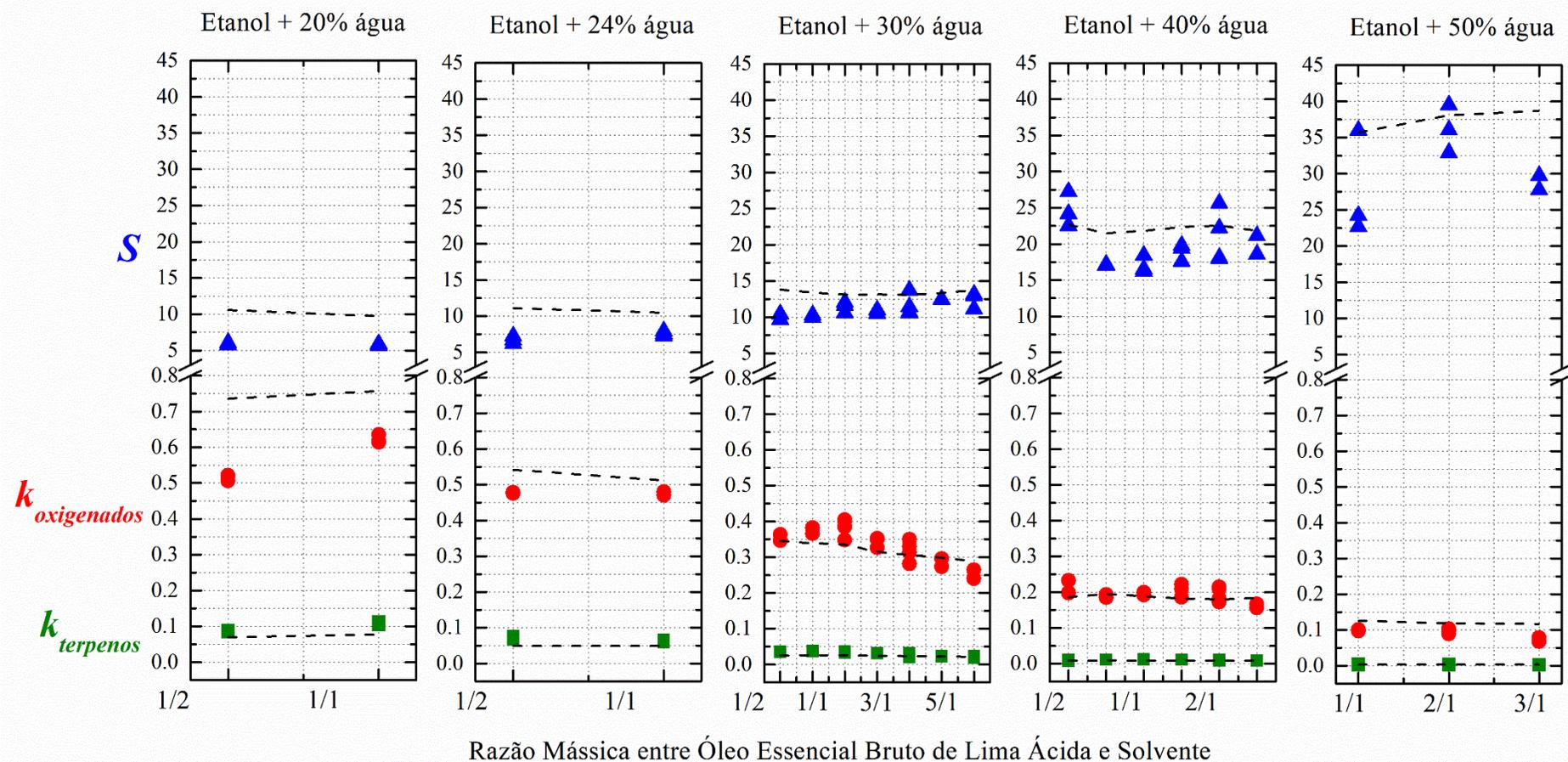
#### V.3.2. Liquid–liquid equilibrium experimental and predicted data

In Table 3 the systems compositions were expressed in mass fractions of terpenes ( $w_1$ ), oxygenated compounds ( $w_2$ ), ethanol ( $w_3$ ), and water ( $w_4$ ), at  $298.2 \pm 0.1$  K, for the different water contents in the solvents [20, 24, 30, 40, and 50% (w/w)] and EO/S ratios (1/2, 1/1.5, 1/1, 1.5/1, 2/1, 3/1, 4/1, and 5/1). The experimental data were validated by relative deviations ( $\delta$ ) lower than 0.5% [26]. Additionally, the tie lines exhibited good repeatability for each EO/S ratio used in the OC. To better understand the LLE data, the partition coefficients of terpenes ( $k_1$ ) and oxygenated compounds ( $k_2$ ) [Eq. (4)] and the solvent selectivity for the oxygenated compounds ( $S$ ) [Eq. (5)] are shown in Fig. 1. According to this data, it is possible to verify that, in general, the higher water content in the solvent led to decreased  $k_1$  and  $k_2$  values and increased  $S$ , which indicates a lower migration of both types of components to the extract phase but also indicates a higher solvent preference for the oxygenated compounds. Higher  $k$  values are

associated with systems with higher phase solubility, and, conversely, higher water content in the system causes lower solubility between the phases.

In fact, the terpenes are insoluble in water, while the oxygenated compounds are partially soluble [33,34], leading to less migration of terpenes than oxygenated compounds into the extract phase, which means that  $k_1$  is less than  $k_2$ . This behavior was also observed in several other studies, including model and real systems of different EOs [9,18,23,25,35–39]. Since the fractionation of EOs are conducted to separate the components,  $k_1$  must values be low, while the  $k_2$  must values be high, denoting higher  $S$  values. As can be verified in Fig. 1, all  $S$  values were higher than 1.0, meaning that the solvent favors the oxygenated compounds independently of its water content or EO/ $S$ .

In general, higher EO/ $S$  values led to lower  $k_1$  and  $k_2$  values but a small increase in  $S$ . These changes to  $S$  are mainly related to changes in  $k_1$ , since the amount of terpenes in the system is much greater than the amount of oxygenated compounds. For the systems composed of crude orange essential oil (COEO), ethanol, and water at  $298.2 \pm 0.1$  K reported by Gonçalves et al. [18], the same tendency was observed. Calculated LLE data using the NTRL parameters from Koshima et al. [9] are also shown in Fig. 1 as dashed lines. The interaction parameters were able to describe the partition of terpenes and oxygenated compounds between the phases and their solvent selectivities.



**Fig. 1** - Distribution coefficients of terpenes ( $k_1$ ) and oxygenated compounds ( $k_2$ ), and solvent selectivity ( $S$ ), at  $T = 298.2.0 \pm 0.1$  K, in relation to the crude acid lime essential oil/ solvent mass ratio (EO/S). Experimental:  $\blacksquare$ ,  $k_1$ ;  $\bullet$ ,  $k_2$ ;  $\blacktriangle$ ,  $S$ . Predicted by the NRTL model using binary parameters from Koshima et al. [9]: - - -. Water mass percentages in the solvent: (a) 20%, (b) 24%, (c) 30%, (d) 40%, and (e) 50%.

Table 4 displays the deviation calculated for each system (different solvents), for each component or group, and the global deviation of the prediction. The good performance of the predictions from the NRTL model is proved by the low global deviation ( $\Delta w = 0.02$ ). Lower deviations were calculated for systems using more hydrated solvents [50% (w/w) water,  $\Delta w = 0.01$ ], while better estimates were achieved for the mass fractions of the oxygenated compounds ( $\Delta w = 0.002$ ) (Table 4).

According to these results, although the CALEO is a complex mixture of terpenes and oxygenated compounds (Table 2), it can be modelled as a limonene/citral mixture, which simplifies the prediction procedures. This approach was successfully applied by Gonçalves et al. [18] in the prediction of the LLE phase compositions from the systems composed of COEO, ethanol and water at  $298.2 \pm 0.1$  K, in which the COEO was considered as a binary mixture of limonene (as terpenes) and linalool (as oxygenated compounds).

The determination of LLE data is a primary study that allows the evaluation of the viability and behavior of industrial separation processes. According to the experimental LLE data, the fractionation of CALEO can be successfully used to acquire extract phases that are enriched in oxygenated compounds. Therefore, to better understand the industrial application of this process, the CALEO was subjected to the fractionation process using continuous equipment (PRDC).

**Table 4:** Mean deviations between experimental and calculated compositions of the systems.

Water in the solvent (% w/w)	$\Delta w^a$
20%	0.04
24%	0.03
30%	0.03
40%	0.02
50%	0.01
Component/ group	
Terpenes (1)	0.03
Oxygenated compounds (2)	0.002
Ethanol (3)	0.03
Water (4)	0.02
Global deviation	0.02

<sup>a</sup> Calculated by Eq. (3).

### V.3.3. Fractionation of crude acid lime essential oil using continuous equipment

#### V.3.3.1. Process performance

Although several hydroalcoholic solvents were used for the determination of LLE data, for the fractionation trials in PRDC only solvents with 40% and 50% (w/w) water were employed (as explained in section 3.3.2). The indices calculated for evaluating the fractionation process are presented in Table 5. For comparison purposes, the results obtained by Gonçalves et al. [22] for COEO are also exhibited in the table.

The global error for the assays using 40% (w/w) water was 0.77%, while for 50% (w/w) water it was 0.90%. The relative errors in the mass balance of a specific component were up to 7.39%, with higher deviations calculated for minor components like the oxygenated compounds. In general, the global and relative errors were below 10%, which is appropriate for continuous processes [22]. The extraction indices are directly related to  $k_i$  and  $S$  (from the LLE data), and it was thus expected that high water content would significantly decrease the % $EXT_{TERP}$  and % $EXT_{OXYG}$  values, since less of the terpenes and oxygenated compounds would migrate into the extract phase (lower  $k$  values). On the other hand, higher water content is associated with higher  $S$  values, and it was observed that % $OE$  increased when solvent with 50% (w/w) water was used, which means that more oxygenated compounds than terpenes were in the extract phase. According to the LLE data, it can be verified that higher water content in the OC led to less migration of solvent (ethanol and water) into the raffinate phase (Table 3), and the PRDC process using solvent with 50% (w/w) water thus yielded a decreased % $M_{SOLV}$  value. Finally, since higher % $OE$  was calculated for the more hydrated solvent [50% water (w/w)], the  $Folds$  increased with higher water contents. The  $Folds$  number is an important parameter for the industry that corresponds to the increased concentration of oxygenated compounds in the fractionated EO. According to the literature [40], fractionating processes of CALEO are applied aiming at 2 – 5-fold. This range was reached and even surpassed: 6-fold for solvent with 40% (w/w) water and 8-fold for 50% (w/w).

Gonçalves et al. [22] used a PRDC for COEO fractionation, with solvents with 30% and 40% (w/w) water, and observed similar trends in the extraction indices (Table 5). Comparing the assays using the same solvent [ethanol 40% (w/w) water, Table 5], for the CALEO reached similar values for % $EXT_{TERP}$  and % $EXT_{OXYG}$ , but lower  $Folds$  were observed for CALEO than for COEO. On the other hand, higher % $M_{SOLV}$  and % $OE$  values were calculated for the CALEO. This can be explained by the fact that the CALEO has more oxygenated compounds in its composition ([7.63 ± 0.07% (w/w)] in relation to the COEO [1.44 ± 0.03% (w/w)]. As in the

LLE, the higher amount of oxygenated compounds in the system led to less migration of these components to the extract phase and an enhanced migration of terpenes, as well as a higher transference of solvent into the raffinate phase (increased % $M_{SOLV}$  value).

Although the CALEO has more oxygenated compounds than the COEO, their  $K_{E-a}$  values in solvent with 40% (w/w) water were equivalent. This may be explained by the partition coefficient of the oxygenated compounds ( $k_2$ ). Since the  $k_2$  for the COEO systems [0.20 – 0.28 [18]] it is expected that fewer oxygenated compounds in CALEO are transferred from the raffinate to the extract phase, denoting lower  $K_{E-a}$  values. Furthermore, as also observed by Gonçalves et al. [22], higher water content in the solvent led to lower  $K_{E-a}$  values.

**Table 5:** Extraction indices for the fractionation of crude acid lime and orange essential oils in PRDC.<sup>a</sup>

% (w/w) Water in the solvent	% $EXT_{TERP}$	% $EXT_{OXYG}$	% $OE$	% $M_{SOLV}$	$Folds$	$K_{E-a} \times 10$
Crude acid lime essential oil (CALEO)						
40.4 ± 0.3%	1.8 ± 0.1 <sup>B</sup>	23 ± 3 <sup>B</sup>	51.8 ± 0.9 <sup>B</sup>	5.2 ± 0.2 <sup>A</sup>	6.8 ± 0.1 <sup>D</sup>	3.4 ± 0.4 <sup>B</sup>
51.2 ± 0.5%	0.48 ± 0.04 <sup>C</sup>	11 ± 1 <sup>C</sup>	65.14 ± 0.01 <sup>A</sup>	4.1 ± 0.2 <sup>B</sup>	8.5 ± 0.1 <sup>C</sup>	1.5 ± 0.1 <sup>C</sup>
Crude orange essential oil (COEO) <sup>b</sup>						
30.2 ± 0.2%	4.5 ± 0.2 <sup>A</sup>	55 ± 3 <sup>A</sup>	14 ± 2 <sup>D</sup>	2.47 ± 0.09 <sup>C</sup>	10.7 ± 0.5 <sup>B</sup>	4.8 ± 0.1 <sup>A</sup>
39.7 ± 0.3%	1.48 ± 0.02 <sup>B</sup>	28 ± 1 <sup>B</sup>	22 ± 1 <sup>C</sup>	2.5 ± 0.3 <sup>C</sup>	15.1 ± 0.2 <sup>A</sup>	3.2 ± 0.9 <sup>B</sup>

The same uppercase letters in the same column indicates no significant difference by Duncan's test ( $P \leq 0.05$ );

<sup>a</sup> Standard uncertainty  $u$  is expressed after each mean value;

<sup>b</sup> Extraction indices from Gonçalves et al. [22].

### V.3.3.2. Physical properties

The physical properties of the output streams (raffinate and extract phases), such as density ( $\rho$ , kg·m<sup>-3</sup>), dynamic viscosity ( $\eta$ , mPa·s) and surface tension ( $\sigma$ , mN·m<sup>-1</sup>) are shown in Table 6. The extract phases exhibited higher density and viscosity than the raffinate phases for both solvents, possibly due to their higher water content. No significant changes to the physical properties of the raffinate phases were observed, while the properties of the extract phases significantly increased with additional water in the solvent. According to Florido et al. [41], higher levels of water in the solvent are related to higher viscosity and density values, especially in the extract phases. In the case of density, water has the highest value (997.04 kg·m<sup>-3</sup>, Table 1), while water, in the presence of ethanol, increases the viscosity of the mixture (reaching a maximum value in a solution with a 0.54 mass fraction of water) [42], which was also observed

in the eucalyptus model system studied by Gonçalves et al. [25]. Comparing the values related to CALEO to those determined by Gonçalves et al. [22] in solvent with 40% water, the absolute differences between the densities ( $\Delta\rho$ ) and between the dynamic viscosities of the phases ( $\Delta\eta$ ) were smaller for CALEO, possibly due to the higher concentration of oxygenated compounds in the raffinate phases. It was already observed that these oxygenated compounds increase the density and viscosity of the mixture [25,41]. Since the amount of oxygenated compounds is higher in the raffinate phases than in the extract, as can be observed in the LLE data (Table 3), the  $\Delta\rho$  and  $\Delta\eta$  become lower.

The extract phases had similar surface tensions to the ones determined for the hydroalcoholic solvents (Table 1), while those for the raffinate phases were similar to the terpenes ( $27 \text{ mN}\cdot\text{m}^{-1}$ ). Interestingly, it was not possible to obtain results from the assays using ethanol with 30% (w/w) water as solvent, probably due to the physical properties of the phases. It was observed that lower water content in the solvent led to lower differences between the densities ( $\Delta\rho$ ) and viscosities ( $\Delta\eta$ ) (Table 6), which made the efficient separation of the phases in the PRDC more difficult. Additionally, due to the phases' similar surface tensions, drops of the dispersed phase (raffinate) were not well established using ethanol with 40% (w/w) water as solvent.

According to the aforementioned discussion, ethanol with 50% (w/w) water is the solvent best suited for the fractionation of CALEO using the PRDC, since it caused the physical properties of the output streams to be more different (Table 6), which enhances the process in this equipment. Furthermore, more *Folds* were calculated for this solvent, and less solvent migrated to the raffinate stream (Table 5).

**Table 6:** Physical properties of the output streams for the fractionation of crude acid lime and orange essential oils in PRDC.<sup>a</sup>

% (w/w) Water in the solvent	Density ( $\rho$ , in $\text{kg}\cdot\text{m}^{-3}$ )			Dynamic Viscosity ( $\eta$ , in $\text{mPa}\cdot\text{s}$ )			Surface Tension ( $\sigma$ , in $\text{mN}\cdot\text{m}^{-1}$ )		
	Raffinate	Extract	$\Delta\rho^b$	Raffinate	Extract	$\Delta\eta^c$	Raffinate	Extract	$\Delta\sigma^d$
	Crude acid lime essential oil (CALEO)								
40.4 $\pm$ 0.3%	857.4 $\pm$ 0.9 <sup>B</sup>	891 $\pm$ 2 <sup>B</sup>	33.5 $\pm$ 0.6 <sup>C</sup>	1.148 $\pm$ 0.003 <sup>A</sup>	2.17 $\pm$ 0.01 <sup>B</sup>	1.02 $\pm$ 0.02 <sup>D</sup>	27 $\pm$ 2 <sup>A</sup>	26.7 $\pm$ 0.1 <sup>B</sup>	1.0 $\pm$ 0.1 <sup>B</sup>
51.2 $\pm$ 0.5%	859.3 $\pm$ 0.1 <sup>A</sup>	914.6 $\pm$ 0.5 <sup>A</sup>	55.3 $\pm$ 0.6 <sup>A</sup>	1.160 $\pm$ 0.002 <sup>A</sup>	2.30 $\pm$ 0.05 <sup>A</sup>	1.14 $\pm$ 0.05 <sup>B</sup>	25.3 $\pm$ 0.1 <sup>A</sup>	28.09 $\pm$ 0.05 <sup>A</sup>	2.8 $\pm$ 0.1 <sup>A</sup>
	Orange Essential Oil (COEO)								
30.2 $\pm$ 0.2%	837.8 $\pm$ 0.1 <sup>C</sup>	863.3 $\pm$ 0.1 <sup>D</sup>	25.5 $\pm$ 0.1 <sup>D</sup> *	0.91 $\pm$ 0.01 <sup>B</sup>	1.99 $\pm$ 0.01 <sup>C</sup>	1.08 $\pm$ 0.01 <sup>C</sup> *	25.00 $\pm$ 0.01 <sup>A</sup>	25.49 $\pm$ 0.02 <sup>D</sup>	0.49 $\pm$ 0.02 <sup>C</sup>
39.7 $\pm$ 0.3%	838.5 $\pm$ 0.1 <sup>C</sup>	887 $\pm$ 2 <sup>C</sup>	49 $\pm$ 2 <sup>B</sup> *	0.86 $\pm$ 0.01 <sup>C</sup>	2.14 $\pm$ 0.01 <sup>B</sup>	1.28 $\pm$ 0.01 <sup>A</sup> *	26 $\pm$ 2 <sup>A</sup>	26.4 $\pm$ 0.1 <sup>C</sup>	1.0 $\pm$ 0.1 <sup>B</sup>

The same uppercase letters in the same column indicates no significant difference by Duncan's test ( $P \leq 0.05$ );

<sup>a</sup> Standard uncertainty is expressed after each mean value;

<sup>b</sup> Absolute difference between the experimental densities of the phases;

<sup>c</sup> Absolute difference between the experimental dynamic viscosities of the phases;

<sup>d</sup> Absolute difference between the experimental surface tensions of the phases;

\* Data from Gonçalves et al. [22].

#### **V.4. Conclusions**

The fractionation of CALEO using ethanol/water mixtures as solvents was possible, and extract phases enriched in oxygenated compounds were achieved. The water content in the solvent is an important parameter for the fractionation of essential oils by liquid–liquid extraction with ethanol/water as the solvent. Increased hydration of the alcoholic solvent is related to lower migration of the components from the raffinate (terpene-rich phase) to the extract (solvent-rich phase), but higher solvent selectivity for the oxygenated compounds was reached. Conversely, increased the mass ratios of the CALEO in the solvent lead to lower partition coefficients. For the experimental LLE data of the systems composed of CALEO, ethanol, and water at  $298.2 \pm 0.1$  K, the same tendency was verified. The predicted composition of the LLE phases from the literature NRTL parameters exhibited satisfactory results, and lower deviations were calculated for the oxygenated compounds group (0.002 mass fraction). Additionally, considering the terpenes and oxygenated compounds as groups provided a good description of their partition coefficients and solvent selectivity values. For the CALEO fractionation in PRDC, more water in the solvent lowered the extraction of terpenes and oxygenated compounds but increased the folds [6-fold using ethanol with 40% water and 8-fold using 50% (w/w) water]. Additionally, higher density, dynamic viscosity, and surface tension were measured in the extract phases with 50% (w/w) water solvent, denoting higher  $\Delta\rho$ ,  $\Delta\eta$ , and  $\Delta\sigma$  values. Therefore, 50% (w/w) water solvent exhibited the best conditions for the process and is the most promising solvent for use in the fractionation of CALEO using PRDC.

#### **V.Acknowledgments**

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## CHAPTER VI: Physical behavior of the phases from the liquid–liquid equilibrium of citrus essential oils systems at 298.2 K.

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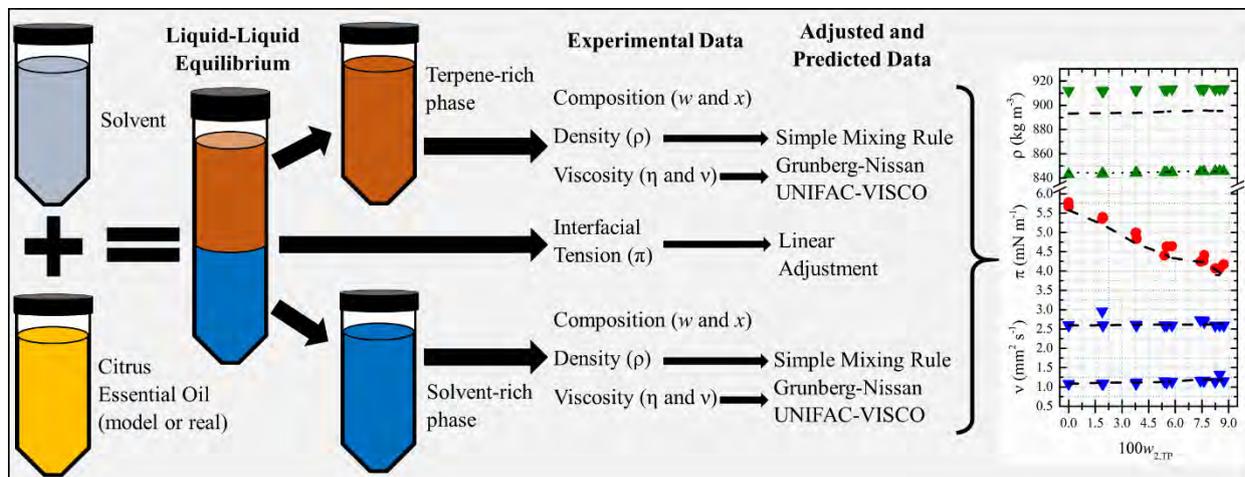
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### VI. Graphical abstract



### VI. Highlights

- Fractionation of orange and acid lime essential oils;
- Densities, viscosities and interfacial tensions of phases were evaluated;
- Water led to higher density, viscosity and interfacial tension values;
- Oxygenated compounds led to lower interfacial tension values;
- Empirical models provided good results on the prediction of physical properties.

## VI. Abstract

Solvent extraction is a fractionation process applied to the separation between terpenes and oxygenated compounds from citrus essential oils (EOs). Knowledge of the physical properties of phases is crucial for equipment design and the scaling of tubes and accessories. This study focused on the evaluation of density, viscosity and interfacial tension of phases from the liquid–liquid equilibrium of citrus EOs systems. Model mixtures of orange (limonene, linalool, ethanol, and water) and lemon/lime (limonene,  $\beta$ -pinene,  $\gamma$ -terpinene, citral, ethanol, and water) EOs and real systems (crude EO, ethanol, and water) at 298.2 K were prepared, and the physical properties of their phases were evaluated. The increase of water content in the solvent led to higher values of density, viscosity, and interfacial tension, while an increase in amount of oxygenated compounds caused lower interfacial tensions. Densities were estimated by the simple mixing rule, which provided good results. Data from the model systems were used to adjust parameters of the Grunberg–Nissan model, which were employed to predict the viscosities of real systems, and low deviations were calculated. The UNIFAC–VISCO model provided suitable predictions of viscosities of the solvent phases. Interfacial tensions of the model systems were correlated to phase compositions by linear adjustment, from which the parameters were used to calculate the interfacial tensions of real systems. The parameters adjusted for the orange model system described the interfacial tension of the real system well. Nonetheless, the adjustment was not efficient for the acid lime real system.

Keywords: orange essential oil, acid lime essential oil, Grunberg–Nissan, UNIFAC–VISCO, viscosity, interfacial tension.

## VI.1. Introduction

Essential oils (EOs) are important commodities in the international market. These raw materials are widely used in cosmetics, pharmaceuticals, and food and beverage formulations [1,2]. In 2015, the total value in EO exportation reached US \$4.71 billion [3]. This year, Brazil was ranked the main EO exporter, at 52.7 thousand tons, denoting US \$339 million in trade [4]. Currently, Brazil is the main exporter of orange EOs, being responsible for 36% of the world's exports [3], and has a slight but important participation in the lemon and lime EO markets [3–5].

Citrus EOs, such as orange, lemon, acid lime, and bergamot, are predominantly composed of volatile components, subdivided into terpene hydrocarbons and oxygenated compounds. Several studies have demonstrated the importance and the technical evaluation of the fractionation of citrus EOs, focusing on the separation between terpenes and oxygenated compounds by liquid–liquid extraction, using ethanol/water mixtures as solvents [1,2,6–9]. From this fractionation process, a product with improved sensorial qualities, stability and solubility in aqueous solutions may be obtained.

Limonene is the main terpene found in citrus EOs, while the composition of the oxygenated fraction is highly varied. For example, the oxygenated fraction of orange EO (varieties Valencia and Pera Rio) is mainly composed of aldehydes (octanal and citronellal) and alcohols (linalool) [1,6], and acid lime and lemon EOs are more abundant in aldehydes (citral) [2,9], while bergamot EO is rich in alcohol (linalool) and ester (linalyl acetate) [8]. The amount of terpenes and oxygenated compounds is also variable depending on the EO. The volatile fraction of orange EO is composed of approximately 1.27% (*w/w*) oxygenated compounds [1], and that of acid lime EO is composed of 7.8% (*w/w*) [2], while that of bergamot EO is composed of approximately 57% (*w/w*) [8]. The composition of the raw material has a direct relation with the partition of the components and the solvent selectivity in a fractionation process by liquid–liquid extraction, as was previously demonstrated in different systems, such as orange [6], lemon [9], acid lime [2], bergamot [8], and other EOs such as lavandin [8], eucalyptus [10], oregano [11], and mint [12]. The composition of the phases from the fractionation also has a direct contribution to the physical properties, such as density and viscosity, as was observed by Florido et al. [7] for bergamot, lemon and mint model systems, and by Gonçalves et al. [10] for eucalyptus model systems. The understanding of the values of physical properties is important for planning and scaling tubes, accessories and industrial equipment as well as for process optimization [13]. Another interesting property for separation processes by liquid–liquid extraction is the tension in the interface between phases (interfacial tension), which is related to the stability of the dispersed phase drops and the efficiency of the phase separation in equipment operations [14].

This study aimed to evaluate the chemical composition of phases from the liquid–liquid equilibrium of citrus EOs over the behavior of their physical properties. The main EOs exported by Brazil, orange (*Citrus sinensis* L. Osbeck) and acid lime (*Citrus latifolia* Tanaka), were the focuses of this work. Model mixtures of orange (limonene, linalool, ethanol, and water) and lemon/lime (limonene,  $\beta$ -pinene,  $\gamma$ -terpinene, citral, ethanol, and water) EOs and real systems (crude orange or acid lime EO, ethanol, and water) were prepared at 298.2 K, and the physical properties of their phases were evaluated. The experimental data of the model systems were used to adjust parameters of empirical models, which were used to predict the viscosity and interfacial tension of real systems. All densities were estimated by the simple mixing rule.

## **VI.2. Materials and methods**

### **VI.2.1. Solvents and reagents**

Hydroalcoholic solvents with different water content were prepared by diluting deionized water (Millipore, Milli-Q, USA) in absolute ethanol. Crude orange (*C. sinensis*) and acid lime (*C. latifolia*) EOs were obtained by cold pressing and were kindly donated by the Louis Dreyfus Company (Bebedouro/SP, Brazil). Limonene, linalool, ethanol, and water were used to prepare the orange model systems, as proposed by Gonçalves et al. [6], while limonene,  $\beta$ -pinene,  $\gamma$ -terpinene, citral, ethanol, and water were used for the lemon/lime model systems, as proposed by Koshima et al. [9]. For the real systems, crude orange EO or crude acid lime EO, ethanol, and water were mixed. The CAS registry numbers, suppliers and experimental purities, sources and experimental physical properties of the standards used for the model systems as well as of the hydroalcoholic solvents and the crude EOs at 298.2 K are shown in Table 1.

**Table 1:** Molar masses ( $M_i$ , in  $\text{g}\cdot\text{mol}^{-1}$ ), CAS numbers, suppliers and experimental purities, source and experimental density ( $\rho$ , in  $\text{kg}\cdot\text{m}^{-3}$ ), dynamic viscosity ( $\eta$ , in  $\text{mPa}\cdot\text{s}$ ), kinematic viscosity ( $\nu$ , in  $\text{mm}^2\cdot\text{s}^{-1}$ ), and surface tension ( $\sigma$ , in  $\text{mN}\cdot\text{m}^{-1}$ ) of standards, solvents, and crude essential oils at  $T = 298.2\text{ K}$  and  $p = 1 \times 10^5\text{ Pa}$ .<sup>†</sup>

Material	$M_i$	CAS number	Supplier Purity	Experimental Purity <sup>a</sup>	Source	$\rho$	$\eta$	$\nu$	$\sigma^b$
<i>Standards</i>									
Water	18.02	7732-18-5				997.04 <sup>*</sup>	0.873 <sup>*</sup>	0.875	71.1 <sup>*</sup>
Ethanol	46.07	64-17-5	0.998	0.999	Merck, Germany	785.18 <sup>*</sup>	1.056 <sup>*</sup>	1.345	21.6 <sup>*</sup>
Octanal	128.2	124-13-0	0.950	0.950	Sigma-Aldrich, USA	835.00	2.757	3.302	23.0
1-Octanol	130.2	111-87-5	0.980	0.990	Sigma-Aldrich, USA	821.70	7.642	9.300	23.5
<i>p</i> -Cymene	134.2	99-87-6	0.970	0.970	Sigma-Aldrich, USA	853.24	0.777	0.911	27.4
( <i>R</i> )-(+)-Limonene	136.2	5989-27-5	0.970	0.988	Sigma-Aldrich, USA	841.35 <sup>*</sup>	0.916 <sup>*</sup>	1.089	27.6 <sup>*</sup>
(-)- $\beta$ -Pinene	136.2	18172-67-3	0.990	0.999	Sigma-Aldrich, USA	866.95 <sup>*</sup>	1.531 <sup>*</sup>	1.766	27.0
$\gamma$ -Terpinene	136.2	99-85-4	0.970	0.977	Sigma-Aldrich, USA	845.16 <sup>*</sup>	0.852	1.008	25.3
(+)- $\alpha$ -Pinene	136.2	232-087-8	0.990	0.990	Sigma-Aldrich, USA	854.69	1.284	1.502	25.9
Citral (neral + geranial)	152.2	5392-40-5	0.960	0.990	Sigma-Aldrich, USA	884.84 <sup>*</sup>	1.930	2.181	31.9
Linalool	154.3	78-70-6	0.970	0.992	Sigma-Aldrich, USA	857.38 <sup>*</sup>	4.565 <sup>*</sup>	5.324	25.4 <sup>*</sup>
( $\pm$ )-Citronellal	154.3	106-23-0	0.980	0.990	Sigma-Aldrich, USA	855.40 <sup>*</sup>	1.688 <sup>*</sup>	1.973	22.5
$\alpha$ -Terpineol	154.3	98-55-5	0.900	0.900	Sigma-Aldrich, USA	931.15	37.32	40.08	31.5
Geraniol	154.3	106-24-1	0.970	0.970	Sigma-Aldrich, USA	874.22	6.690	7.652	30.2
Decanal	156.3	112-31-2	0.950	0.950	Sigma-Aldrich, USA	838.37	3.039	3.625	24.4
<i>Solvents<sup>c</sup></i>									
0.508 $\pm$ 0.002	31.92					911.41	2.235	2.452	28.2
0.426 $\pm$ 0.005	34.13					890.10 <sup>*</sup>	2.180 <sup>*</sup>	2.450	26.7 <sup>*</sup>
0.311 $\pm$ 0.003	37.36					865.50 <sup>*</sup>	1.799 <sup>*</sup>	2.079	25.6 <sup>*</sup>
0.247 $\pm$ 0.001	39.22					850.50	1.798	2.114	25.3
0.235 $\pm$ 0.002	39.22					847.41	1.731	2.043	25.1
0.206 $\pm$ 0.008	39.24					841.91	1.676	1.990	24.8
<i>Crude Essential Oils</i>									
Orange ( <i>C. sinensis</i> )					Louis Dreyfus Company, Brazil	841.08 <sup>*</sup>	0.903 <sup>*</sup>	1.074	24.8 <sup>*</sup>
Ternepe group <sup>d</sup>	136.2					841.67	0.925	1.099	
Oxygenated group <sup>d</sup>	145.1					849.83	3.438	4.048	
Acid Lime ( <i>C. latifolia</i> )					Louis Dreyfus Company, Brazil	864.57	1.234	1.427	25.3
Ternepe group <sup>d</sup>	137.7					845.40	1.006	1.187	
Oxygenated group <sup>d</sup>	155.4					873.35	4.000	4.415	

<sup>†</sup> Standard uncertainties  $u$  are  $u(T) = 0.1\text{ K}$ ,  $u(p) = 1 \times 10^3\text{ Pa}$ ,  $u(\rho) = 0.01\text{ kg}\cdot\text{m}^{-3}$ ,  $u(\eta) \leq 0.07\text{ mPa}\cdot\text{s}$ ,  $u(\nu) \leq 0.07\text{ mm}^2\cdot\text{s}^{-1}$ , and  $u(\sigma) \leq 0.1\text{ mN}\cdot\text{m}^{-1}$ ;

<sup>a</sup> Determined by GC-FID, given as mass fraction ( $w_i$ ), without further purification;

<sup>b</sup> Surface tension of standards in concordance to the value reported by Jasper [23];

<sup>c</sup> Water content in ethanol, given as mass fraction followed by the standard uncertainty;

<sup>d</sup> Values calculated considering the composition of each pure component in the group and its respective physical property;

<sup>\*</sup> Experimental data in agreement with values previously reported in the literature [1,6,7,10].

## VI.2.2. Experimental procedures

### VI.2.2.1. Standards purities

The purities and retention times of standards were assessed using a gas chromatograph with a flame ionization detector (GC-FID, Shimadzu, model GC 2010 AF, Japan) and an automatic injector (Shimadzu, model AOC 20i, Japan). The capillary column used was a nitroterephthalic acid-modified polyethylene glycol (DB-FFAP,  $0.25 \times 10^{-6}$  m capillary thickness, 30 m length,  $0.25 \times 10^{-3}$  m internal diameter; Agilent, USA), and the analysis conditions were the same as adopted in previous studies [1,2,6,10]: helium as the carrier gas at  $1.13 \text{ mL}\cdot\text{min}^{-1}$ , 523.2 K injection temperature and  $1 \times 10^{-3}$  mL injection volume with a 50:1 split ratio, a column temperature program from 373.2 to 513.2 K (at  $8 \text{ K}\cdot\text{min}^{-1}$ ) and held at 513.2 K for 1 min (18.5 min each analysis), and 553.2 K of detection temperature. Samples were diluted in 1-propanol (99.9%, Sigma-Aldrich, EUA) with 1:1 mass ratio before GC-FID analysis.

### VI.2.2.2. Chemical characterization of the crude essential oils

The chemical composition of the volatile fraction of crude orange (*C. sinensis*) and acid lime (*C. latifolia*) EOs was performed in a gas chromatograph coupled to a mass spectrometer (GC-MS, Shimadzu, model QP 2010 Plus, Japan) with an automatic injector (Shimadzu, model AOC-5000, Japan). The capillary column and analysis conditions were the same as the ones adopted for GC-FID analysis (section 2.2.1). The column interface temperature was 518.2 K, the ion source temperature was 473.2 K, and mass spectral scanning ranged from 40 to 800 m/z with 70 eV of ion source energy according to the procedure described by Gonçalves et al. [6]. Samples were diluted in 1-propanol with a 1:1 mass ratio before GC-MS analysis. The components were identified via comparison with standards retention times and/or by similarity of the component mass spectra with the one contained in the Solutions GC-MS software (version 2.5, NIST 08 and NIST 08s libraries) and/or by comparison with the Kovats retention index ( $KI_i$ ) calculated for each component with the one from the literature [6,8] for the same DB-FFAP capillary column. For  $KI_i$  determination [Eq. (1)], the alkane standards  $C_{10}$ – $C_{40}$  (Sigma-Aldrich, USA) were analyzed under the same GC-MS conditions.

$$KI_i = 100 \cdot C_{i-1} + 100 \cdot \left[ \frac{\log RT_i - \log RT_{i-1}}{\log RT_{i+1} - \log RT_{i-1}} \right] \quad (1)$$

where  $C_{i-1}$  is the number of carbons in the alkane immediately preceding the analyte,  $RT_i$  is the analyte retention time,  $RT_{i-1}$  is the retention time of the alkane immediately preceding the analyte, and  $RT_{i+1}$  is the retention time of the alkane immediately after the analyte.

The mass fraction of the components identified in the crude EOs was calculated by internal normalization in the GC-FID analysis, and components with mass fractions lower than 0.001 were not considered.

### VI.2.2.3. Liquid–liquid equilibrium

The liquid–liquid equilibrium (LLE) was reached according to a method adopted for several EO systems [2,6,8–12,15,16]. For the orange model systems, different mass proportions between limonene and linalool were prepared and contacted with the hydroalcoholic solvent (ethanol with 23, 30, or 40% water) using a mass ratio of 1:1. For the lime/lemon model systems, a stock solution composed of limonene,  $\beta$ -pinene, and  $\gamma$ -terpinene was prepared and mixed with citral at different mass proportions, then contacted with the solvent (ethanol with 30, 40, or 50% water) using the same 1:1 mass ratio. For the real systems, the crude EO was contacted with the solvent (ethanol with 30 or 40% water for orange EO, and ethanol with 20, 24, 30, 40, or 50% water for acid lime EO) in different mass ratios (1:2, 1:1.5, 1:1, 1.5:1, 2:1, 3:1, 4:1, 5:1) depending on the solvent used.

The mixtures were prepared in a capped polypropylene tube (15 or 50 mL, Corning, USA), and the masses were measured using an analytical balance (Adam, PW Model 254, USA, accurate to 0.0001 g). The tubes were vigorously agitated at 2800 rpm for 10 minutes at room temperature ( $298 \pm 1$  K), centrifuged for 30 min at 5000 g and a controlled temperature of  $298.2 \pm 1.5$  K (Thermo Electron Corporation, model CR3i, France) and maintained in a thermostatic bath (Marconi, model MA-184, Brazil) at  $298.2 \pm 0.1$  K for 20 h to produce LLE. After that, two homogeneous and well-formed phases were obtained, the terpene-rich and the solvent-rich phase, which were separately collected by syringes. The composition in terms of terpenes, oxygenated compounds, and ethanol was assessed by GC-FID analysis, while the water content was determined by Karl Fischer titration (Metrohm, 787 KF Titrino, Switzerland) using Karl Fischer reagents (CombiTitrant 5 mg H<sub>2</sub>O·mL<sup>-1</sup>, Merck, Germany). The physical properties of the LLE phases were measured as described in the next section.

As adopted in previous studies [2,6], terpenes and oxygenated compounds were grouped for the real systems; therefore, the LLE data were presented in terms of terpenes (1), oxygenated compounds (2), ethanol (3), and water (4). Standard uncertainties Type A [17] were estimated in the LLE data to be less than or equal to 0.001 mass fraction.

#### VI.2.2.4. Physical properties

Standards, hydroalcoholic solvents, crude EOs, and phases from the LLE were submitted for experimental determination of their physical properties, such as density ( $\rho$ , in  $\text{g}\cdot\text{cm}^{-3}$ ), dynamic viscosity ( $\eta$ , in  $\text{mPa}\cdot\text{s}$ ), and kinematic viscosity ( $\nu$ , in  $\text{mm}^2\cdot\text{s}^{-1}$ ). The surface tension ( $\sigma$ , in  $\text{mN}\cdot\text{m}^{-1}$ ) of the crude EOs, solvents and standards, and the interfacial tension between the LLE phases ( $\pi$ , in  $\text{mN}\cdot\text{m}^{-1}$ ) was also measured.

Densities were measured in a bench digital densimeter (Anton Paar, model DMA 4500, Austria) at  $298.2 \pm 0.1$  K in triplicate, with experimental uncertainties not exceeding  $1 \times 10^{-5}$   $\text{g}\cdot\text{cm}^{-3}$ . Dynamic viscosities were determined in a falling ball automated micro viscometer (Anton Paar, model AMVn, Austria) at  $298.2 \pm 0.1$  K at three inclination angles (50, 60, and 70°). The measurement was repeated four times for each inclination angle, yielding a total of twelve measurements per sample, according to the procedure conducted by Gonçalves et al. [10]. Kinematic viscosities were calculated by dividing the dynamic viscosity by the density ( $\nu = \eta/\rho$ ). The uncertainties were estimated to be less than or equal to 0.07  $\text{mPa}\cdot\text{s}$  for dynamic viscosity and 0.07  $\text{mm}^2\cdot\text{s}^{-1}$  for kinematic viscosity.

Surface and interfacial tensions were evaluated using a force tensiometer (Attension, model Sigma 702, Finland) at  $298.2 \pm 0.1$  K. The surface tension was measured in triplicate, and the experimental uncertainty reached 0.1  $\text{mN}\cdot\text{m}^{-1}$ . The sample was placed inside a glass vessel, and a platinum Du Noüy ring submerged the sample until the higher tension registered [6]. For the determination of interfacial tension between the solvent and terpene phases, the heavy phase (predominantly the solvent-rich phase) was first placed in a glass vessel, and the Du Noüy ring was immersed within that phase. The light phase (predominantly the terpene-rich phase) was then slowly placed above the heavy phase so that the LLE was not lost. Then, the ring made an upward movement and the equipment indicated the interfacial tension when the higher tension value was reached. The uncertainty for the interfacial tension was up to 0.01  $\text{mN}\cdot\text{m}^{-1}$ . All standard uncertainties were estimated by Type A [17].

### VI.2.3. Correlation and prediction

#### VI.2.3.1. Density

Density ( $\rho$ , in  $\text{g}\cdot\text{cm}^{-3}$ ) of each pure component was calculated by GCVOL model [18], by Eq. (2).

$$\rho_i^{calc} = \frac{M_i}{V_i} = \frac{M_i}{\sum_{j=1}^K n_j \cdot \Delta v_j} \quad (2)$$

where  $MM_i$  is the molar mass of the component  $i$  ( $\text{g}\cdot\text{mol}^{-1}$ ),  $V_i$  is the molar volume ( $\text{cm}^3\cdot\text{mol}^{-1}$ ),  $K$  is the total number of GCVOL groups,  $n_j$  is the amount of each GCVOL group  $j$  appearing in the component  $i$ , and  $\Delta v_j$  is the group volume increment ( $\text{cm}^3\cdot\text{mol}^{-1}$ ), calculated by Eq. (3).

$$\Delta v_j = A_j + B_j \cdot T + C_j \cdot T^2 \quad (3)$$

where  $A$ ,  $B$ , and  $C$  are the GCVOL-60 parameters of each group  $j$  in the molecule  $i$ , from Ihmels and Gmehling [18], and  $T$  is the temperature (298.2 K).

The density of the mixtures (crude EOs, phases from the LLE, and solvents) were estimated using the simple mixing rule [Eq. (4)], in mass and molar basis.

$$\rho^{calc} = \sum_{i=1}^N c_i \cdot \rho_i \quad (4)$$

where  $c_i$  is either the mass fraction ( $w_i$ ) or the molar fraction ( $x_i$ ) of the component  $i$ ,  $N$  is the number of components in the mixture, and  $\rho_i$  is the density of the pure component  $i$ .

To evaluate the complexity of the mixtures, the excess molar volume ( $V^E$ , in  $\text{cm}^3\cdot\text{mol}^{-1}$ ) was calculated by Eq. (5). Small relative deviations in the density by the simple mixing rule are related to lower  $V^E$  values [10].

$$V^E = \sum_{i=1}^N x_i \cdot M_i \cdot \left( \frac{1}{\rho} - \frac{1}{\rho_i} \right) \quad (5)$$

where  $N$  is the total number of components in the mixture,  $x_i$  is the molar fraction of the component  $i$ ,  $M_i$  is the molar mass of component  $i$  ( $\text{g}\cdot\text{mol}^{-1}$ ),  $\rho$  is the mixture density, and  $\rho_i$  is the density of the pure component  $i$ . For the crude essential oils, the  $\rho_i$  of terpenes and oxygenated compounds group were estimated by weight, considering the molar fraction of each component in the group and its density.

### VI.2.3.2. Viscosity

The experimental viscosity values of the LLE phases from the model systems were used to adjust the interaction parameters of the Grunberg–Nissan model in Eq. (6) [19]. Although the original equation is for dynamic viscosity ( $\eta$ , in  $\text{mPa}\cdot\text{s}$ ) and compositions in molar fraction ( $x_i$ ), in this study we also considered kinematic viscosity ( $\nu$ ,  $\text{mm}^2\cdot\text{s}^{-1}$ ) and compositions in mass fraction ( $w_i$ ).

$$\ln D^{calc} = \sum_{i=1}^N c_i \cdot \ln D_i + \frac{1}{2} \cdot \sum_{i=1}^N \sum_{\substack{j=1 \\ j \neq i}}^N c_i \cdot c_j \cdot G_{ij} \quad (6)$$

where  $D$  can be assumed as dynamic ( $\eta$ ) or kinematic viscosity ( $\nu$ ),  $c_i$  is either the molar fraction ( $x_i$ ) or the mass fraction ( $w_i$ ) of the component  $i$  or  $j$  ( $i \neq j$ ),  $D_i$  is the experimental  $\eta$  or  $\nu$  of component  $i$ ,  $N$  is the number of components in the mixture, and  $G_{ij}$  is the binary interaction parameter, adjusted by Matlab® software (MathWorks, version R2015a, USA).

The  $G_{ij}$  values adjusted for the model systems were used to calculate the viscosity of the LLE phases of both model and real systems at 298.2 K. For the orange real system, the terpene group was considered as limonene, while the oxygenated group was assumed as linalool, according to the approach adopted by Gonçalves et al. [6]. For the acid lime real system, the oxygenated group was considered as citral, while the terpene group was also considered as limonene, as assumed by Gonçalves et al. [2]. For that, other parameters were adjusted for the lemon/lime model system counting the terpenes ( $\beta$ -pinene, limonene, and  $\gamma$ -terpinene) as limonene, i.e.,  $c_{terpenes} = c_{\beta\text{-pinene}} + c_{limonene} + c_{\gamma\text{-terpinene}}$  ( $c$  can be either mass or molar fraction). The kinematic viscosity of all LLE phases (from the model and real systems) was also predicted by the UNIFAC-VISCO model [20,21] using the parameters adjusted by Florido et al. [7] and the compositions in molar fraction.

### VI.2.3.3. Interfacial Tension

The tensions between the LLE phases ( $\pi$ , in  $\text{mN}\cdot\text{m}^{-1}$ ) of the model systems (orange and lemon/lime EOs) were correlated to phase compositions according to Eq. (7), adapted from Treybal [22]. Although the original equation refers to the composition in molar fraction, the mass fraction was also considered.

$$\pi^{calc} = a - b \cdot \ln(c_{terpenes,SP} + c_{oxygenated,SP} + c_{ethanol,TP} + c_{water,TP}) \quad (7)$$

where  $a$  and  $b$  were correlated by a least-squares fitting procedure by Origin Pro® software (OriginLab, version 90E, USA),  $c$  can be either the molar fraction ( $x_i$ ) or the mass fraction ( $w_i$ ) of the component  $i$  (terpenes, oxygenated compounds, ethanol, or water), and the subscripts  $SP$  and  $TP$  correspond to solvent-rich and terpene-rich phases, respectively. The parameters  $a$  and  $b$ , adjusted to the model systems, were used to calculate the interfacial tension of the real systems.

### VI.2.3.4. Evaluation of calculated data

To evaluate the quality of the correlated and calculated physical properties, the average relative deviations ( $\Delta$ , in %) were calculated following Eq. (8).

$$\Delta = \frac{100}{N} \cdot \sum_{i=1}^N \frac{|y_i^{\text{exp}} - y_i^{\text{calc}}|}{y_i^{\text{exp}}} \quad (8)$$

where  $y$  can be assumed as density ( $\rho$ ), dynamic viscosity ( $\eta$ ), kinematic viscosity ( $\nu$ ), or interfacial tension ( $\pi$ ); the superscripts exp and calc correspond to the experimental and calculated physical property, respectively;  $i$  is the value referring to the phase; and  $N$  is the total number of experimental data points.

### VI.3. Results and discussion

#### VI.3.1. Crude EOs characterization

Table 2 presents the compositions of the crude orange and acid lime EOs in mass fraction ( $w_i$ ) and molar fraction ( $x_i$ ), as well as the molar fraction of each component in the terpene or oxygenated group ( $x_j$ ), and the physical properties of some components identified in these oils (standards). The chemical characterization of the crude EOs is in agreement with previous studies [2,6]. The terpene fraction of orange EO is mainly composed of *d*-limonene (97.6%) and  $\alpha$ -pinene (2.4%), while the acid lime EO is a complex mixture of hydrocarbons, predominantly *d*-limonene (63.4%),  $\gamma$ -terpinene (15.5%),  $\beta$ -pinene (13.9%), and  $\alpha$ -pinene (2.9%) ( $w/w$ ). The oxygenated fraction of acid lime EO is four times that of orange EO (4.4% and 1.1%, respectively), and their compositions are also different. The acid lime EO oxygenated fraction is more abundant in citral (geranial 53.7%, and neral 26.6%), while the orange EO contains linalool (37.8%), octanal (28.4%), and citronellal (21.2%) ( $w/w$ ).

The density of each pure component calculated by the GCVOL model [Eq. (2)] is also shown in Table 2. The relative deviations between experimental and calculated values [Eq. (8)] were from 0.31 to 1.81%, demonstrating good agreement with experimental values. Therefore, the GCVOL model is a worthy tool to predict the density values of pure components. The densities and viscosities of terpenes and oxygenated groups of real systems were calculated using the  $x_j$  composition and the property of each pure component. For the components for which the density was not experimentally determined, the calculation by the GCVOL model was considered. The calculated density and viscosity values of the terpene and oxygenated groups are shown in Table 1.

**Table 2:** Chemical characterization of crude orange and acid lime essential oils, retention times (RT), identification procedure, molar masses ( $M_i$ , in  $\text{g}\cdot\text{mol}^{-1}$ ), Kovats Index ( $KI_i$ ), compositions in mass fraction ( $w_i$ ) and molar fraction ( $x_i$ ), and calculated density by GCVOL model ( $\rho_i^{\text{CALC}}$ , in  $\text{g}\cdot\text{cm}^{-3}$ ), at  $T = 298.2$  K and  $p = 1 \times 10^5$  Pa.<sup>†</sup>

Component ( <i>i</i> )	RT	$KI_i^b$	Identification <sup>a</sup>	$M_i$	Crude Orange Essential Oil			Crude Acid Lime Essential Oil			$\rho_i^{\text{CALC } d}$
					$w_i$	$x_i$	$x_i^c$	$w_i$	$x_i$	$x_i^c$	
<i>Terpenes</i>					0.987	0.990	1.000	0.956	0.961	1.000	
$\alpha$ -Pinene	2.58	1487	Standard/ $KI^*$	136.2	0.024	0.024	0.024	0.027	0.027	0.029	862.14
$\beta$ -Pinene	2.47	1479	Standard/ $KI^*$	136.3				0.131	0.133	0.139	856.97
Myrcene	2.55	1485	NIST-MS	136.3				0.014	0.014	0.015	772.40
$d$ -Limonene	2.91	1604	Standard/ $KI^*$	136.2	0.963	0.966	0.976	0.600	0.609	0.634	853.93
$\gamma$ -Terpinene	3.02	1617	Standard/ $KI^*$	136.2				0.146	0.149	0.155	853.93
$p$ -Cymene	3.13	1624	Standard/ $KI^*$	134.2				0.001	0.001	0.001	855.89
Terpinolene	3.19	1628	NIST-MS	136.2				0.007	0.007	0.007	908.78
$\delta$ -Elemene	4.58	1802	NIST-MS	204.4				0.001	0.001	0.001	770.76
$\beta$ -Caryophyllene	5.76	1860	NIST-MS/ $KI^*$	204.4				0.012	0.008	0.008	954.62
$\beta$ -Elemene	6.01	1871	NIST-MS	204.4				0.005	0.003	0.003	836.03
$\alpha$ -Bergamotene	6.56	1894	NIST-MS	204.4				0.001	0.001	0.001	1093.1
$\beta$ -Farnesene	6.82	1904	NIST-MS/ $KI^*$	204.4				0.001	0.000	0.000	814.05
$\beta$ -Bisabolene	7.39	2034	NIST-MS/ $KI^*$	204.4				0.010	0.007	0.007	808.91
$\beta$ -Germacrene	7.89	2057	NIST-MS	204.4				0.001	0.000	0.000	817.03
<i>Oxygenated Compounds</i>					0.011	0.010	1.000	0.044	0.039	1.000	
Octanal	3.23	1630	Standard/ $KI^*$	128.2	0.003	0.003	0.284				819.92
Decanal	4.83	1815	Standard/ $KI^*$	156.3				0.001	0.000	0.012	826.28
Citronellal	4.89	1819	Standard/ $KI^*$	154.3	0.003	0.002	0.212				850.03
Linalool	5.24	1837	Standard/ $KI^*$	154.2	0.004	0.004	0.378	0.002	0.002	0.047	850.59
Octanol	5.35	1842	Standard/ $KI^*$	130.2	0.001	0.001	0.067				824.27
Neral	6.95	2012	Standard/ $KI^*$	152.2				0.011	0.010	0.266	872.33
$\alpha$ -Terpineol	7.01	2015	Standard/ $KI^*$	154.3				0.002	0.002	0.048	937.95
Geranial	7.59	2042	Standard/ $KI^*$	152.2	0.001	0.001	0.059	0.023	0.021	0.537	872.33
Geranyl Acetate	7.68	2047	NIST-MS/ $KI^*$	196.3				0.002	0.001	0.036	593.72
Geraniol	8.20	2070	Standard/ $KI^*$	154.3				0.001	0.001	0.034	875.75
Bisabolol	8.72	2092	NIST-MS/ $KI^*$	222.4				0.001	0.001	0.018	835.09

<sup>†</sup> Standard uncertainties  $u$  are  $u(T) = 0.1$  K,  $u(p) = 1 \times 10^3$  Pa,  $u(w) \leq 0.001$ ,  $u(x) \leq 0.001$ ,  $u(\eta) \leq 0.07$  mPa·s,  $u(\nu) \leq 0.07$  mm<sup>2</sup>·s<sup>-1</sup>,  $u(\sigma) \leq 0.1$  mN·m<sup>-1</sup>, and  $u(\rho) = 0.01$  kg·m<sup>-3</sup>;

<sup>a</sup> Identified by GC-MS (NIST-MS library), and by comparison with the standard retention time and/or with  $KI$  values from the literature;

<sup>b</sup> Calculated by Eq. (1);

<sup>c</sup> Composition of the component  $i$  in the group terpenes or oxygenated compounds;

<sup>d</sup> Calculated by Eq. (2), in kg·m<sup>-3</sup>;

\* Kovats Index in agreement with value previously reported in the literature [6,8].

### VI.3.2. LLE experimental data

The LLE data of the model systems are shown in Table 3 for orange EO and in Table 4 for lemon/lime EOs. The LLE data of the real systems are shown in Table 5 for orange EO and in Table 6 for acid lime EO. The crude EO compositions were represented by terpenes (1) and oxygenated compounds (2) groups. The physical properties ( $\rho$ ,  $\eta$ , and  $\nu$ ), the excess volumes ( $V^E$ ) of each phase, and the interfacial tensions ( $\pi$ ) are also presented in these tables.

**Density and viscosity:** In all model or real systems, the increased water content in the phases led to higher density and dynamic viscosity values, mainly for the solvent phases, which are rich in ethanol and water. We can also observe in Table 1 that increasing water in the solvents led to higher physical property values. Increasing the amount of oxygenated compounds in the phases also related to higher density and viscosity values, since these components have higher viscosities and, in general, higher density values (Tables 1 and 2). The experimental data of lemon/lime model systems are in agreement with reports by Florido et al. [7], and the same tendencies were observed in bergamot [7], mint [7] and eucalyptus [10] model systems.

**Interfacial tension:** For orange and lemon/lime model systems (Tables 3 and 4, respectively) and for the orange real system (Table 5), the increased water content in the solvent also led to higher interfacial tension values. This can be attributed to the fact that water has the highest surface tension value ( $71.1 \text{ mN}\cdot\text{m}^{-1}$ , Table 1) and decreases the solubility between the LLE phases [1,6,8–10,12,16], contributing to higher interfacial tension values. However, the increase in interfacial tensions of the acid lime real system with increasing water was less prominent than in the model system. Conversely, an increasing amount of oxygenated compounds was related to lower interfacial tension values, since these components increase the solubility of the phases [6,10,12].

**Table 3:** Liquid–liquid equilibrium data for orange essential oil model systems composed of limonene (1), linalool (2), ethanol (3), and water (4), in mass fractions ( $w$ ), density ( $\rho$ , in  $\text{g}\cdot\text{cm}^{-3}$ ), dynamic viscosity ( $\eta$ , in  $\text{mPa}\cdot\text{s}$ ), kinematic viscosity ( $\nu$ , in  $\text{mm}^2\cdot\text{s}^{-1}$ ), and excess volume ( $V^E$ , in  $\text{cm}^3\cdot\text{mol}^{-1}$ ) of the phases, and interfacial tension ( $\pi$ , in  $\text{mN}\cdot\text{m}^{-1}$ ) at  $T = 298.2\text{ K}$  and  $p = 1 \times 10^5\text{ Pa}$ .<sup>a</sup>

$w_{4,S}^b$	Overall Composition (OC)				Terpene-rich Phase (TP)								Solvent-rich Phase (SP)								$\pi$
	$w_1$	$w_2$	$w_3$	$w_4$	$w_1$	$w_2$	$w_3$	$w_4$	$\rho$	$\eta$	$\nu$	$V^E$	$w_1$	$w_2$	$w_3$	$w_4$	$\rho$	$\eta$	$\nu$	$V^E$	
$0.235 \pm 0.002$	0.500		0.387	0.113	0.979		0.019	0.002	837.38	0.811	1.051	0.58	0.074		0.712	0.215	847.34	1.717	1.947	-0.60	2.18
	0.501		0.386	0.113	0.964		0.033	0.003	837.30	0.821	1.004	0.44	0.074		0.707	0.218	847.15	1.694	1.967	-0.60	2.34
	0.500		0.387	0.113	0.965		0.033	0.002	837.33	0.858	0.998	0.42	0.073		0.706	0.221	847.18	1.698	1.984	-0.63	2.39
	0.493	0.005	0.388	0.114	0.959	0.004	0.035	0.002	836.64	0.818	0.991	0.53	0.072	0.006	0.706	0.216	846.27	1.695	1.973	-0.46	2.30
	0.495	0.005	0.385	0.115	0.960	0.004	0.033	0.002	836.48	0.812	0.996	0.58	0.071	0.006	0.704	0.220	846.08	1.686	1.992	-0.47	2.22
	0.495	0.005	0.385	0.115	0.955	0.004	0.039	0.003	836.48	0.829	0.992	0.53	0.072	0.006	0.695	0.228	846.08	1.685	2.037	-0.55	2.28
	0.490	0.010	0.385	0.115	0.954	0.008	0.036	0.002	836.36	0.848	0.992	0.58	0.073	0.012	0.693	0.221	846.32	1.694	2.016	-0.54	2.08
	0.490	0.010	0.385	0.115	0.955	0.008	0.034	0.003	836.99	0.816	1.003	0.49	0.070	0.012	0.694	0.224	847.38	1.708	2.027	-0.71	2.12
	0.490	0.010	0.385	0.115	0.955	0.008	0.035	0.003	836.48	0.815	1.003	0.58	0.071	0.012	0.697	0.219	847.16	1.713	2.002	-0.64	2.22
	0.484	0.015	0.385	0.115	0.947	0.012	0.038	0.003	836.33	0.810	0.998	0.58	0.075	0.018	0.686	0.221	846.40	1.716	2.029	-0.56	2.00
	0.485	0.015	0.386	0.114	0.945	0.012	0.040	0.003	836.39	0.832	0.997	0.56	0.079	0.018	0.688	0.215	846.50	1.716	1.993	-0.52	2.00
	0.484	0.015	0.386	0.114	0.946	0.012	0.039	0.003	836.43	0.841	0.994	0.56	0.076	0.018	0.691	0.214	846.62	1.716	1.992	-0.53	1.83
	0.478	0.020	0.387	0.114	0.939	0.016	0.042	0.003	836.39	0.854	0.992	0.55	0.080	0.024	0.680	0.215	846.56	1.723	2.013	-0.55	1.68
	0.479	0.020	0.386	0.114	0.936	0.016	0.045	0.003	836.34	0.832	0.980	0.52	0.077	0.024	0.685	0.214	846.56	1.717	2.006	-0.54	1.67
	0.477	0.020	0.388	0.115	0.938	0.016	0.043	0.003	836.45	0.830	0.990	0.53	0.079	0.024	0.687	0.210	846.59	1.713	1.982	-0.50	1.69
$0.311 \pm 0.003$	0.500		0.342	0.159	0.976		0.022	0.002	837.31	0.852	1.033	0.54	0.034		0.651	0.315	864.69	1.986	2.312	-3.61	3.29
	0.500		0.341	0.159	0.975		0.022	0.003	837.33	0.866	1.048	0.56	0.017		0.659	0.323	865.75	1.941	2.285	-3.78	3.24
	0.493	0.005	0.353	0.149	0.966	0.005	0.026	0.003	837.29	0.823	1.030	0.52	0.037	0.005	0.664	0.294	866.49	1.922	2.251	-3.75	2.92
	0.494	0.005	0.352	0.149	0.972	0.005	0.021	0.003	837.38	0.863	1.059	0.58	0.033	0.005	0.673	0.289	862.54	2.126	2.234	-3.22	2.75
	0.479	0.005	0.366	0.151	0.969	0.005	0.024	0.002	837.40	0.887	1.027	0.51	0.040	0.005	0.678	0.277	862.14	1.879	2.199	-3.10	2.76
	0.490	0.010	0.351	0.148	0.962	0.010	0.026	0.003	837.22	0.917	1.034	0.55	0.039	0.010	0.652	0.299	863.59	1.904	2.295	-3.41	2.52
	0.488	0.010	0.352	0.150	0.963	0.010	0.024	0.003	837.24	0.837	1.049	0.58	0.041	0.011	0.661	0.288	862.20	1.893	2.259	-3.18	2.47
	0.487	0.010	0.354	0.149	0.945	0.010	0.042	0.003	837.28	0.883	0.983	0.37	0.038	0.010	0.660	0.292	862.45	1.892	2.269	-3.23	2.52
	0.485	0.016	0.341	0.159	0.950	0.016	0.031	0.003	837.58	0.877	1.027	0.46	0.032	0.016	0.638	0.314	866.54	2.000	2.336	-3.86	2.37
	0.477	0.015	0.347	0.162	0.951	0.015	0.031	0.004	837.68	0.871	1.037	0.45	0.038	0.015	0.637	0.310	866.40	1.996	2.338	-3.83	2.43
	0.485	0.015	0.350	0.150	0.946	0.015	0.036	0.003	837.68	0.871	1.010	0.39	0.038	0.014	0.654	0.294	864.83	1.983	2.280	-3.56	2.36
	0.479	0.020	0.352	0.149	0.942	0.020	0.036	0.003	837.29	0.860	1.014	0.47	0.036	0.020	0.654	0.289	862.55	1.913	2.277	-3.25	2.12
	0.479	0.020	0.352	0.149	0.946	0.019	0.033	0.002	837.39	0.895	1.012	0.46	0.046	0.021	0.648	0.285	862.88	1.952	2.284	-3.27	2.06
	0.479	0.020	0.352	0.149	0.951	0.017	0.029	0.003	837.38	0.837	1.036	0.52	0.045	0.023	0.646	0.286	862.97	1.942	2.292	-3.29	2.03
	0.474	0.025	0.342	0.159	0.934	0.025	0.037	0.004	837.53	0.910	1.027	0.45	0.039	0.024	0.629	0.308	866.51	2.025	2.357	-3.85	2.11
0.475	0.025	0.341	0.159	0.933	0.026	0.037	0.003	837.63	0.909	1.017	0.41	0.038	0.023	0.623	0.315	867.52	2.027	2.378	-4.00	2.05	
0.475	0.025	0.350	0.150	0.928	0.026	0.043	0.003	837.30	0.870	0.993	0.40	0.041	0.024	0.639	0.296	865.30	2.025	2.319	-3.64	2.14	

$w_{4,S}^b$	Overall Composition (OC)				Terpene-rich Phase (TP)								Solvent-rich Phase (SP)								$\pi$
	$w_1$	$w_2$	$w_3$	$w_4$	$w_1$	$w_2$	$w_3$	$w_4$	$\rho$	$\eta$	$\nu$	$V^E$	$w_1$	$w_2$	$w_3$	$w_4$	$\rho$	$\eta$	$\nu$	$V^E$	
$0.426 \pm 0.005$	0.500		0.281	0.219	0.981		0.016	0.002	837.68	0.862	1.060	0.55	0.009		0.550	0.441	888.24	2.196	2.387	-6.61	4.57
	0.500		0.286	0.214	0.981		0.017	0.002	837.78	0.821	1.048	0.51	0.011		0.568	0.421	891.97	2.170	2.371	-6.99	4.58
	0.477	0.005	0.305	0.213	0.978	0.006	0.014	0.002	837.78	0.819	1.071	0.57	0.011	0.004	0.592	0.393	889.80	2.176	2.349	-6.75	3.80
	0.495	0.005	0.295	0.205	0.973	0.006	0.019	0.001	837.88	0.816	1.043	0.49	0.011	0.004	0.587	0.399	889.97	2.168	2.356	-6.77	3.68
	0.494	0.005	0.295	0.205	0.973	0.006	0.019	0.002	838.20	0.875	1.054	0.44	0.011	0.003	0.580	0.406	890.45	2.136	2.365	-6.83	3.78
	0.490	0.010	0.290	0.210	0.965	0.013	0.020	0.002	837.95	0.830	1.047	0.48	0.012	0.008	0.562	0.418	888.90	2.146	2.405	-6.67	3.62
	0.490	0.010	0.289	0.211	0.958	0.014	0.026	0.003	837.81	0.868	1.039	0.46	0.012	0.007	0.562	0.420	888.98	2.148	2.399	-6.68	3.54
	0.490	0.010	0.295	0.205	0.965	0.013	0.020	0.002	838.35	0.732	1.050	0.42	0.010	0.006	0.576	0.408	890.80	2.148	2.368	-6.87	3.42
	0.485	0.015	0.286	0.214	0.953	0.019	0.025	0.003	837.40	0.826	1.050	0.56	0.013	0.010	0.549	0.428	892.21	2.193	2.415	-7.01	3.47
	0.485	0.015	0.286	0.214	0.952	0.019	0.027	0.003	837.40	0.835	1.042	0.54	0.012	0.010	0.560	0.418	892.11	2.177	2.398	-7.00	3.48
	0.485	0.016	0.294	0.205	0.949	0.021	0.029	0.002	837.40	0.835	1.024	0.51	0.012	0.010	0.575	0.404	892.11	2.177	2.379	-7.00	3.49
	0.474	0.026	0.286	0.214	0.931	0.033	0.032	0.003	837.36	0.843	1.043	0.54	0.011	0.014	0.547	0.429	892.73	2.211	2.408	-7.07	3.01
	0.472	0.025	0.287	0.215	0.931	0.034	0.032	0.004	837.45	0.859	1.049	0.53	0.013	0.016	0.537	0.435	892.60	2.211	2.434	-7.06	2.99
	0.470	0.025	0.298	0.208	0.929	0.033	0.036	0.003	837.36	0.843	1.018	0.48	0.012	0.014	0.565	0.409	892.60	2.211	2.393	-7.06	3.03
	0.465	0.035	0.295	0.205	0.904	0.047	0.045	0.004	837.85	0.863	1.026	0.37	0.013	0.021	0.549	0.417	891.44	2.187	2.430	-6.94	2.50
	0.464	0.035	0.295	0.206	0.902	0.047	0.047	0.005	837.75	0.858	1.024	0.37	0.012	0.020	0.551	0.417	891.45	2.184	2.423	-6.94	2.51
	0.460	0.035	0.302	0.203	0.912	0.050	0.035	0.004	838.17	0.909	1.053	0.42	0.013	0.020	0.560	0.407	892.14	2.214	2.413	-7.01	2.45

<sup>a</sup> Standard uncertainties  $u$  are  $u(T) = 0.1$  K,  $u(p) = 1 \times 10^3$  Pa,  $u(w) \leq 0.001$ ,  $u(\rho) = 0.01$  kg·m<sup>-3</sup>,  $u(\eta) \leq 0.07$  mPa·s,  $u(\nu) \leq 0.07$  mm<sup>2</sup>·s<sup>-1</sup>, and  $u(\pi) \leq 0.01$  mN·m<sup>-1</sup>;

<sup>b</sup> Water mass fraction in the solvent, followed by the standard uncertainty.

**Table 4:** Liquid–liquid equilibrium data for lemon/lime model systems composed of  $\beta$ -pinene (1), limonene (2),  $\gamma$ -terpinene (3), citral (4), ethanol (5), and water (6), in mass fractions ( $w$ ), density ( $\rho$ , in  $\text{kg}\cdot\text{m}^{-3}$ ), dynamic viscosity ( $\eta$ , in  $\text{mPa}\cdot\text{s}$ ), kinematic viscosity ( $\nu$ , in  $\text{mm}^2\cdot\text{s}^{-1}$ ), and excess volume ( $V^E$ , in  $\text{cm}^3\cdot\text{mol}^{-1}$ ) of the phases, and interfacial tension ( $\pi$ , in  $\text{mN}\cdot\text{m}^{-1}$ ) at  $T = 298.2\text{ K}$  and  $p = 1 \times 10^5\text{ Pa}$ .<sup>a</sup>

$w_{4,S}^b$	Overall Composition (OC)					Terpene-rich Phase (TP)								Solvent-rich Phase (SP)								$\pi$			
	$w_1$	$w_2$	$w_3$	$w_4$	$w_5$	$w_1$	$w_2$	$w_3$	$w_4$	$w_5$	$\rho$	$\eta$	$\nu$	$V^E$	$w_1$	$w_2$	$w_3$	$w_4$	$w_5$	$\rho$	$\eta$		$\nu$	$V^E$	
0.311 ±																									
0.003	0.075	0.340	0.084		0.153	0.145	0.661	0.162		0.031	842.12	0.875	1.039	2.62	0.003	0.014	0.003		0.670	866.46	1.918	2.213	-1.04	3.29	
	0.074	0.338	0.083		0.152	0.145	0.662	0.162		0.030	842.13	0.866	1.029	2.63	0.003	0.014	0.003		0.675	876.80	1.920	2.190	-1.53	3.30	
	0.074	0.340	0.084		0.155	0.146	0.660	0.161		0.031	842.16	0.867	1.029	2.61	0.003	0.013	0.003		0.667	876.80	1.947	2.220	-1.43	3.24	
	0.073	0.334	0.082	0.010	0.153	0.143	0.647	0.158	0.014	0.036	842.38	0.926	1.100	2.55	0.003	0.015	0.003	0.005	0.666	866.45	1.987	2.293	-1.05	3.04	
	0.073	0.335	0.082	0.010	0.155	0.143	0.646	0.158	0.014	0.037	842.40	0.927	1.100	2.53	0.003	0.013	0.003	0.005	0.665	866.53	1.995	2.302	-1.03	2.97	
	0.073	0.332	0.081	0.010	0.156	0.143	0.647	0.158	0.014	0.036	842.42	0.923	1.095	2.54	0.003	0.014	0.003	0.005	0.665	866.28	1.985	2.291	-1.02	2.91	
	0.072	0.324	0.079	0.020	0.147	0.141	0.628	0.153	0.025	0.051	842.84	0.955	1.133	2.24	0.004	0.019	0.004	0.015	0.678	863.11	2.071	2.399	-1.12	2.60	
	0.072	0.322	0.079	0.020	0.148	0.140	0.629	0.154	0.026	0.049	842.91	0.966	1.146	2.27	0.004	0.018	0.004	0.015	0.667	863.26	2.070	2.398	-1.01	2.63	
	0.072	0.320	0.083	0.020	0.147	0.141	0.619	0.161	0.025	0.051	842.92	0.954	1.132	2.20	0.004	0.018	0.004	0.014	0.672	863.02	2.072	2.401	-1.04	2.56	
	0.070	0.319	0.078	0.030	0.154	0.135	0.612	0.149	0.048	0.052	843.07	0.939	1.114	2.30	0.003	0.013	0.003	0.015	0.658	866.66	1.986	2.291	-1.02	2.50	
	0.071	0.320	0.079	0.030	0.147	0.136	0.616	0.153	0.044	0.048	842.98	0.946	1.122	2.37	0.003	0.013	0.003	0.014	0.680	866.77	1.987	2.292	-1.23	2.45	
	0.069	0.320	0.076	0.040	0.144	0.132	0.608	0.140	0.059	0.057	845.16	0.986	1.166	1.92	0.005	0.024	0.005	0.020	0.662	863.56	2.120	2.455	-1.05	2.18	
	0.069	0.320	0.076	0.040	0.145	0.133	0.613	0.147	0.059	0.044	843.42	0.997	1.182	2.44	0.004	0.019	0.004	0.019	0.671	863.57	2.089	2.420	-1.09	2.17	
	0.069	0.318	0.076	0.039	0.145	0.132	0.607	0.145	0.058	0.054	843.18	0.980	1.163	2.29	0.004	0.033	0.006	0.019	0.654	863.12	2.091	2.423	-1.01	2.17	
	0.067	0.306	0.075	0.051	0.151	0.130	0.588	0.143	0.079	0.056	843.70	0.965	1.143	2.24	0.004	0.017	0.004	0.027	0.645	867.09	2.000	2.307	-1.03	2.05	
	0.067	0.306	0.075	0.051	0.153	0.130	0.586	0.143	0.079	0.057	843.75	0.995	1.179	2.23	0.004	0.017	0.004	0.027	0.638	867.56	1.987	2.290	-0.97	2.08	
	0.067	0.308	0.076	0.050	0.150	0.130	0.589	0.144	0.078	0.057	843.86	0.953	1.129	2.20	0.004	0.017	0.004	0.027	0.649	867.58	2.004	2.310	-1.07	2.07	
0.426 ±																									
0.005	0.075	0.342	0.084		0.201	0.147	0.665	0.162		0.024	842.78	0.901	1.069	2.63	0.001	0.005	0.001		0.587	888.13	2.187	2.463	-1.05	4.16	
	0.075	0.340	0.083		0.201	0.147	0.664	0.163		0.024	842.57	0.890	1.057	2.67	0.001	0.005	0.001		0.588	888.04	2.184	2.459	-1.06	4.25	
	0.075	0.340	0.083		0.202	0.148	0.663	0.165		0.023	842.58	0.893	1.060	2.69	0.001	0.005	0.001		0.589	887.99	2.180	2.455	-1.06	4.28	
	0.071	0.323	0.079	0.010	0.207	0.145	0.649	0.162	0.017	0.026	843.02	0.909	1.078	2.62	0.001	0.006	0.001	0.004	0.586	888.06	2.179	2.454	-1.06	3.87	
	0.073	0.333	0.082	0.010	0.201	0.145	0.647	0.161	0.017	0.028	843.03	0.951	1.129	2.58	0.001	0.006	0.001	0.004	0.590	888.18	2.188	2.463	-1.10	3.88	
	0.074	0.335	0.082	0.010	0.201	0.143	0.644	0.160	0.016	0.035	842.63	0.944	1.120	2.53	0.001	0.006	0.001	0.004	0.578	888.61	2.202	2.478	-1.02	3.78	
	0.070	0.322	0.079	0.020	0.205	0.140	0.634	0.158	0.036	0.031	843.64	0.961	1.139	2.51	0.001	0.004	0.001	0.005	0.583	894.84	2.384	2.664	-1.27	3.92	
	0.067	0.320	0.076	0.020	0.210	0.135	0.644	0.155	0.036	0.027	843.55	0.986	1.168	2.62	0.001	0.004	0.001	0.005	0.578	893.50	2.399	2.685	-1.18	3.96	
	0.070	0.317	0.081	0.020	0.208	0.139	0.634	0.159	0.037	0.029	843.68	1.003	1.188	2.53	0.001	0.004	0.001	0.005	0.579	894.85	2.390	2.671	-1.23	3.91	
	0.069	0.316	0.077	0.030	0.207	0.136	0.611	0.152	0.049	0.047	843.47	0.931	1.104	2.31	0.002	0.007	0.001	0.011	0.572	888.94	2.197	2.472	-1.02	3.26	
	0.070	0.320	0.078	0.031	0.201	0.135	0.606	0.151	0.047	0.056	843.28	0.973	1.154	2.19	0.002	0.007	0.002	0.011	0.574	889.03	2.200	2.474	-1.05	3.28	
	0.071	0.321	0.079	0.030	0.201	0.136	0.610	0.151	0.051	0.047	843.35	0.951	1.127	2.36	0.001	0.006	0.001	0.011	0.574	889.05	2.197	2.472	-1.03	3.25	
	0.069	0.315	0.081	0.040	0.201	0.133	0.598	0.155	0.071	0.041	844.59	1.065	1.261	2.29	0.001	0.005	0.001	0.013	0.560	895.50	2.382	2.660	-1.15	3.34	
	0.067	0.317	0.081	0.040	0.201	0.129	0.602	0.156	0.068	0.044	844.58	0.997	1.180	2.25	0.001	0.004	0.001	0.013	0.565	895.08	2.383	2.662	-1.17	3.36	
	0.068	0.315	0.081	0.040	0.201	0.132	0.598	0.158	0.070	0.040	844.58	0.988	1.170	2.31	0.002	0.004	0.002	0.012	0.566	894.99	2.387	2.667	-1.17	3.37	
	0.070	0.311	0.078	0.049	0.200	0.134	0.588	0.151	0.083	0.042	845.09	1.014	1.199	2.24	0.001	0.004	0.001	0.013	0.567	895.50	2.305	2.574	-1.20	3.20	

$w_{4,S}^b$	Overall Composition (OC)					Terpene-rich Phase (TP)								Solvent-rich Phase (SP)								$\pi$		
	$w_1$	$w_2$	$w_3$	$w_4$	$w_5$	$w_1$	$w_2$	$w_3$	$w_4$	$w_5$	$\rho$	$\eta$	$\nu$	$V^E$	$w_1$	$w_2$	$w_3$	$w_4$	$w_5$	$\rho$	$\eta$		$\nu$	$V^E$
	0.070	0.311	0.078	0.049	0.200	0.131	0.587	0.151	0.088	0.040	845.16	1.004	1.188	2.29	0.001	0.005	0.001	0.012	0.568	895.59	2.414	2.695	-1.21	3.16
	0.070	0.311	0.078	0.050	0.199	0.128	0.591	0.149	0.086	0.043	845.26	1.019	1.205	2.23	0.001	0.004	0.001	0.013	0.563	895.82	2.403	2.683	-1.17	3.23
0.508 ±																								
0.002	0.074	0.336	0.083		0.256	0.147	0.668	0.166		0.017	842.95	0.914	1.084	2.73	0.000	0.001	0.000		0.491	911.83	2.365	2.594	-1.02	5.67
	0.074	0.338	0.083		0.255	0.146	0.669	0.166		0.017	842.94	0.913	1.083	2.74	0.000	0.001	0.000		0.490	911.93	2.363	2.592	-1.01	5.78
	0.074	0.338	0.083		0.255	0.147	0.667	0.165		0.018	842.92	0.916	1.086	2.71	0.000	0.001	0.000		0.488	912.05	2.373	2.601	-1.00	5.74
	0.073	0.334	0.083	0.010	0.252	0.144	0.652	0.163	0.019	0.021	843.47	0.925	1.097	2.65	0.000	0.001	0.000	0.002	0.485	912.33	2.368	2.595	-0.99	5.40
	0.073	0.328	0.081	0.010	0.256	0.146	0.651	0.162	0.019	0.021	843.54	0.918	1.088	2.63	0.000	0.001	0.000	0.002	0.487	911.93	2.697	2.957	-1.00	5.35
	0.074	0.333	0.082	0.010	0.252	0.145	0.652	0.161	0.019	0.020	843.49	0.912	1.081	2.65	0.000	0.001	0.000	0.002	0.487	911.27	2.364	2.595	-0.98	5.38
	0.076	0.328	0.080	0.020	0.250	0.148	0.631	0.156	0.038	0.025	844.15	0.913	1.081	2.50	0.000	0.001	0.000	0.003	0.485	912.60	2.373	2.600	-1.01	5.00
	0.073	0.331	0.081	0.020	0.250	0.141	0.637	0.158	0.038	0.025	844.16	0.936	1.109	2.54	0.000	0.001	0.000	0.004	0.488	912.53	2.388	2.617	-1.03	4.99
	0.073	0.330	0.081	0.020	0.250	0.141	0.636	0.158	0.038	0.025	844.24	0.949	1.124	2.51	0.000	0.001	0.000	0.003	0.480	912.80	2.374	2.601	-0.98	4.84
	0.071	0.324	0.080	0.029	0.250	0.136	0.621	0.154	0.058	0.028	844.70	0.962	1.139	2.48	0.000	0.001	0.000	0.004	0.477	913.40	2.368	2.592	-0.97	4.64
	0.074	0.323	0.079	0.029	0.249	0.142	0.618	0.153	0.054	0.030	844.76	0.972	1.151	2.39	0.000	0.001	0.000	0.004	0.482	913.10	2.370	2.596	-1.00	4.40
	0.071	0.329	0.080	0.030	0.247	0.140	0.621	0.152	0.055	0.030	844.44	0.943	1.117	2.46	0.000	0.002	0.000	0.005	0.478	912.74	2.368	2.595	-0.96	4.63
	0.072	0.323	0.080	0.039	0.245	0.135	0.606	0.153	0.074	0.030	845.11	0.984	1.165	2.42	0.000	0.001	0.000	0.004	0.478	913.49	2.490	2.726	-0.99	4.25
	0.071	0.323	0.080	0.039	0.246	0.133	0.606	0.151	0.076	0.031	845.10	0.989	1.170	2.43	0.000	0.001	0.000	0.005	0.468	913.59	2.448	2.680	-0.91	4.41
	0.071	0.324	0.080	0.039	0.245	0.134	0.605	0.152	0.076	0.031	845.11	0.989	1.170	2.43	0.000	0.001	0.000	0.006	0.479	913.05	2.488	2.724	-0.98	4.27
	0.068	0.328	0.075	0.048	0.242	0.127	0.604	0.141	0.087	0.038	845.44	0.974	1.152	2.34	0.000	0.001	0.000	0.006	0.472	913.45	2.367	2.591	-0.95	4.18
	0.071	0.319	0.078	0.049	0.244	0.133	0.596	0.149	0.082	0.036	845.59	0.962	1.138	2.26	0.000	0.001	0.000	0.008	0.478	913.03	2.366	2.592	-0.99	4.07
	0.071	0.321	0.079	0.049	0.242	0.133	0.597	0.149	0.085	0.032	845.59	1.116	1.320	2.35	0.000	0.001	0.000	0.007	0.474	913.38	2.369	2.594	-0.96	4.07

<sup>a</sup> Standard uncertainties  $u$  are  $u(T) = 0.1$  K,  $u(p) = 1 \times 10^3$  Pa,  $u(w) \leq 0.001$ ,  $u(\rho) = 0.01$  kg·m<sup>-3</sup>,  $u(\eta) \leq 0.07$  mPa·s,  $u(\nu) \leq 0.07$  mm<sup>2</sup>·s<sup>-1</sup>, and  $u(\pi) \leq 0.01$  mN·m<sup>-1</sup>;

<sup>b</sup> Water mass fraction in the solvent, followed by the standard uncertainty.

**Table 5:** Liquid–liquid equilibrium data for systems composed of crude orange essential oil [represented by terpenes (1) and oxygenated compounds (2)], ethanol (3), and water (4), in mass fractions ( $w$ ), density ( $\rho$ , in  $\text{kg}\cdot\text{m}^{-3}$ ), dynamic viscosity ( $\eta$ , in  $\text{mPa}\cdot\text{s}$ ), kinematic viscosity ( $\nu$ , in  $\text{mm}^2\cdot\text{s}^{-1}$ ), and excess volume ( $V^E$ , in  $\text{cm}^3\cdot\text{mol}^{-1}$ ) of the phases, and interfacial tension ( $\pi$ , in  $\text{mN}\cdot\text{m}^{-1}$ ) at  $T = 298.2\text{ K}$  and  $p = 1 \times 10^5\text{ Pa}$ .<sup>a</sup>

$w_{4,S}^b$	Overall Composition (OC)				Terpene-rich Phase (TP)								Solvent-rich Phase (SP)								$\pi$
	$w_1$	$w_2$	$w_3$	$w_4$	$w_1$	$w_2$	$w_3$	$w_4$	$\rho$	$\eta$	$\nu$	$V^E$	$w_1$	$w_2$	$w_3$	$w_4$	$\rho$	$\eta$	$\nu$	$V^E$	
$0.311 \pm 0.003$	0.329	0.005	0.470	0.197	0.960	0.007	0.031	0.002	837.60	0.892	1.065	0.45	0.029	0.004	0.676	0.292	863.04	1.964	2.276	-1.07	2.72
	0.328	0.005	0.470	0.197	0.960	0.007	0.031	0.002	837.84	0.912	1.088	0.40	0.032	0.003	0.671	0.294	862.59	1.964	2.277	-1.02	2.81
	0.332	0.005	0.467	0.196	0.959	0.007	0.031	0.002	837.61	0.911	1.087	0.46	0.029	0.003	0.678	0.290	863.14	1.968	2.280	-1.09	2.77
	0.327	0.005	0.471	0.197	0.960	0.006	0.032	0.002	837.77	0.870	1.039	0.41	0.033	0.004	0.679	0.284	863.28	1.891	2.191	-1.14	2.72
	0.329	0.005	0.470	0.197	0.965	0.009	0.024	0.002	837.67	0.917	1.095	0.52	0.012	0.003	0.691	0.294	863.66	1.989	2.303	-1.11	
	0.490	0.007	0.354	0.148	0.956	0.009	0.033	0.002	838.42	0.915	1.091	0.30	0.028	0.005	0.672	0.295	864.99	1.960	2.266	-1.11	2.74
	0.493	0.007	0.352	0.148	0.956	0.009	0.033	0.002	837.96	0.915	1.092	0.38	0.030	0.005	0.673	0.291	915.90	2.035	2.222	-3.21	2.73
	0.493	0.007	0.350	0.150	0.955	0.009	0.034	0.002	837.81	0.910	1.087	0.39	0.030	0.005	0.667	0.297	864.52	1.993	2.305	-1.07	2.73
	0.656	0.010	0.236	0.099	0.953	0.011	0.034	0.002	837.96	0.915	1.092	0.36	0.026	0.006	0.664	0.304	867.97	2.035	2.344	-1.15	2.66
	0.657	0.009	0.233	0.100	0.953	0.011	0.034	0.002	838.11	0.911	1.086	0.33	0.027	0.006	0.649	0.317	868.81	2.046	2.355	-1.06	2.59
	0.738	0.011	0.176	0.075	0.953	0.012	0.033	0.002	838.17	0.904	1.079	0.34	0.024	0.007	0.652	0.317	871.27	2.082	2.390	-1.16	2.65
	0.739	0.011	0.175	0.075	0.952	0.012	0.034	0.002	838.20	0.914	1.090	0.32	0.024	0.006	0.647	0.323	871.30	2.092	2.401	-1.12	2.63
	0.789	0.011	0.140	0.060	0.953	0.013	0.032	0.002	838.30	0.901	1.075	0.32	0.026	0.007	0.635	0.332	874.33	2.105	2.407	-1.14	
	0.788	0.012	0.141	0.059	0.953	0.013	0.032	0.002	838.24	0.900	1.074	0.34	0.027	0.007	0.647	0.320	874.41	2.106	2.408	-1.26	
0.788	0.011	0.140	0.060	0.952	0.013	0.034	0.002	838.19	0.874	1.043	0.33	0.024	0.006	0.636	0.334	911.80	2.109	2.313	-2.57		
$0.426 \pm 0.005$	0.330	0.005	0.382	0.283	0.965	0.010	0.023	0.002	838.39	0.853	1.018	0.40	0.008	0.002	0.563	0.427	893.66	2.143	2.398	-1.06	3.62
	0.329	0.005	0.392	0.274	0.965	0.009	0.024	0.003	838.22	0.861	1.027	0.44	0.009	0.002	0.578	0.411	893.41	2.154	2.411	-1.19	3.65
	0.493	0.007	0.288	0.211	0.961	0.012	0.025	0.002	838.53	0.866	1.033	0.35	0.007	0.003	0.558	0.432	895.26	2.162	2.415	-1.07	3.50
	0.493	0.007	0.292	0.208	0.963	0.011	0.025	0.001	838.79	0.862	1.027	0.30	0.008	0.003	0.573	0.416	895.41	2.139	2.389	-1.21	3.53
	0.655	0.009	0.195	0.141	0.960	0.012	0.025	0.003	838.78	0.869	1.036	0.33	0.008	0.003	0.553	0.436	897.99	2.184	2.432	-1.13	3.11
	0.657	0.009	0.194	0.139	0.961	0.012	0.025	0.002	838.67	0.856	1.021	0.33	0.008	0.003	0.553	0.436	898.33	2.190	2.438	-1.14	3.18
	0.739	0.011	0.145	0.106	0.957	0.013	0.026	0.003	838.94	0.863	1.029	0.30	0.007	0.003	0.538	0.453	900.97	2.212	2.455	-1.09	3.16
	0.739	0.011	0.146	0.105	0.961	0.013	0.025	0.001	838.89	0.866	1.032	0.29	0.007	0.003	0.541	0.449	901.42	2.210	2.451	-1.14	3.12
	0.739	0.011	0.146	0.105	0.961	0.013	0.025	0.001	838.76	0.854	1.018	0.31	0.008	0.003	0.544	0.445	901.02	2.212	2.455	-1.15	3.04
	0.788	0.011	0.117	0.084	0.961	0.013	0.024	0.002	838.53	0.864	1.031	0.36	0.007	0.003	0.534	0.457	903.78	2.226	2.463	-1.15	
0.788	0.011	0.118	0.082	0.961	0.013	0.024	0.001	839.16	0.864	1.029	0.25	0.006	0.003	0.539	0.452	903.80	2.235	2.472	-1.19		

<sup>a</sup> Standard uncertainties  $u$  are  $u(T) = 0.1\text{ K}$ ,  $u(p) = 1 \times 10^3\text{ Pa}$ ,  $u(w) \leq 0.001$ ,  $u(\rho) = 0.01\text{ kg}\cdot\text{m}^{-3}$ ,  $u(\eta) \leq 0.07\text{ mPa}\cdot\text{s}$ ,  $u(\nu) \leq 0.07\text{ mm}^2\cdot\text{s}^{-1}$ , and  $u(\pi) \leq 0.01\text{ mN}\cdot\text{m}^{-1}$ ;

<sup>b</sup> Water mass fraction in the solvent, followed by the standard uncertainty.

**Table 6:** Liquid–liquid equilibrium data for systems composed of crude acid lime essential oil [represented by terpenes (1) and oxygenated compounds (2)], ethanol (3), and water (4), in mass fractions ( $w$ ), density ( $\rho$ , in  $\text{kg}\cdot\text{m}^{-3}$ ), dynamic viscosity ( $\eta$ , in  $\text{mPa}\cdot\text{s}$ ), kinematic viscosity ( $\nu$ , in  $\text{mm}^2\cdot\text{s}^{-1}$ ), and excess volume ( $V^E$ , in  $\text{cm}^3\cdot\text{mol}^{-1}$ ) of the phases, and interfacial tension ( $\pi$ , in  $\text{mN}\cdot\text{m}^{-1}$ ) at  $T = 298.2\text{ K}$  and  $p = 1 \times 10^5\text{ Pa}$ .<sup>a</sup>

$w_{4,S}^b$	Overall Composition (OC)				Terpene-rich Phase (TP)								Solvent-rich Phase (SP)								$\pi$
	$w_1$	$w_2$	$w_3$	$w_4$	$w_1$	$w_2$	$w_3$	$w_4$	$\rho$	$\eta$	$\nu$	$V^E$	$w_1$	$w_2$	$w_3$	$w_4$	$\rho$	$\eta$	$\nu$	$V^E$	
0.206 ± 0.008	0.310	0.024	0.528	0.138	0.880	0.036	0.078	0.006	851.76	1.104	1.296	-1.56	0.077	0.018	0.711	0.193	846.04	1.797	2.124	-1.12	
	0.310	0.024	0.529	0.137	0.881	0.036	0.077	0.006	851.80	1.117	1.312	-1.56	0.075	0.019	0.716	0.190	846.17	1.782	2.106	-1.16	
	0.310	0.024	0.530	0.137	0.877	0.036	0.081	0.006	851.81	1.122	1.317	-1.60	0.075	0.019	0.715	0.192	846.18	1.692	1.999	-1.15	
	0.463	0.035	0.402	0.100	0.852	0.043	0.099	0.006	854.23	1.144	1.339	-2.06	0.095	0.028	0.688	0.189	849.67	1.722	2.027	-1.27	1.09
	0.465	0.035	0.401	0.099	0.849	0.044	0.100	0.006	853.89	1.136	1.331	-2.01	0.090	0.027	0.693	0.190	849.69	1.718	2.022	-1.28	1.04
0.247 ± 0.001	0.465	0.035	0.400	0.100	0.849	0.044	0.100	0.007	853.82	1.133	1.327	-1.99	0.089	0.027	0.693	0.191	849.66	1.714	2.018	-1.26	1.05
	0.329	0.025	0.488	0.158	0.878	0.039	0.076	0.006	854.98	1.129	1.321	-2.04	0.068	0.019	0.683	0.231	856.47	1.803	2.105	-1.24	
	0.308	0.025	0.504	0.163	0.859	0.038	0.093	0.010	853.67	1.137	1.332	-1.84	0.057	0.018	0.692	0.233	855.67	1.815	2.121	-1.21	
	0.317	0.025	0.498	0.161	0.894	0.039	0.060	0.007	854.72	1.146	1.341	-1.86	0.063	0.019	0.690	0.228	856.01	1.807	2.111	-1.26	
	0.463	0.037	0.377	0.123	0.878	0.050	0.064	0.008	856.12	1.158	1.353	-2.03	0.052	0.024	0.687	0.238	859.09	1.854	2.158	-1.31	1.37
0.311 ± 0.003	0.463	0.037	0.377	0.123	0.878	0.050	0.066	0.006	856.12	1.164	1.360	-2.12	0.058	0.024	0.678	0.240	859.23	1.869	2.175	-1.28	1.20
	0.463	0.037	0.377	0.123	0.869	0.050	0.073	0.008	856.24	1.152	1.346	-2.12	0.055	0.024	0.682	0.238	859.55	1.892	2.201	-1.31	1.45
	0.311	0.023	0.459	0.207	0.897	0.040	0.059	0.004	855.01	1.142	1.336	-1.97	0.031	0.014	0.650	0.305	868.19	1.955	2.251	-1.11	1.84
	0.312	0.023	0.456	0.209	0.900	0.039	0.056	0.004	855.46	1.127	1.317	-2.04	0.032	0.014	0.645	0.309	867.90	1.954	2.251	-1.05	1.87
	0.464	0.032	0.347	0.157	0.894	0.046	0.056	0.005	855.40	1.153	1.348	-1.97	0.033	0.017	0.651	0.298	869.02	1.983	2.282	-1.19	1.71
	0.463	0.033	0.347	0.157	0.894	0.048	0.054	0.005	855.79	1.172	1.370	-2.02	0.033	0.017	0.647	0.302	869.85	1.987	2.284	-1.18	1.78
	0.461	0.035	0.347	0.157	0.887	0.050	0.058	0.005	856.34	1.141	1.333	-2.13	0.032	0.019	0.647	0.302	871.00	1.994	2.289	-1.23	1.48
	0.468	0.036	0.342	0.154	0.871	0.052	0.073	0.005	856.30	1.166	1.361	-2.22	0.029	0.018	0.644	0.310	871.59	2.037	2.337	-1.19	1.58
	0.465	0.035	0.344	0.155	0.883	0.050	0.062	0.005	856.12	1.153	1.347	-2.11	0.030	0.020	0.640	0.310	871.18	2.014	2.311	-1.16	1.50
	0.465	0.035	0.345	0.155	0.883	0.050	0.063	0.004	856.44	1.167	1.362	-2.19	0.030	0.020	0.637	0.313	871.34	2.033	2.333	-1.14	
	0.619	0.047	0.227	0.107	0.870	0.059	0.065	0.006	857.65	1.165	1.358	-2.32	0.027	0.019	0.610	0.344	876.83	2.053	2.341	-1.07	1.40
	0.616	0.047	0.233	0.105	0.873	0.059	0.061	0.007	857.71	1.184	1.380	-2.27	0.028	0.021	0.635	0.316	877.97	2.095	2.386	-1.38	1.41
	0.617	0.047	0.232	0.104	0.870	0.059	0.066	0.005	857.58	1.178	1.373	-2.33	0.028	0.020	0.628	0.324	876.58	2.071	2.362	-1.26	1.42
	0.693	0.054	0.174	0.079	0.874	0.063	0.058	0.004	858.71	1.176	1.370	-2.47	0.027	0.021	0.614	0.338	881.60	2.110	2.393	-1.31	1.36
	0.692	0.056	0.173	0.079	0.870	0.065	0.060	0.005	858.46	1.183	1.378	-2.42	0.026	0.020	0.599	0.355	881.94	2.113	2.396	-1.17	1.36
0.695	0.055	0.173	0.077	0.870	0.063	0.062	0.005	858.53	1.185	1.380	-2.44	0.027	0.022	0.616	0.335	881.90	2.160	2.450	-1.35		
0.696	0.053	0.173	0.078	0.875	0.062	0.055	0.007	858.88	1.215	1.414	-2.40	0.018	0.018	0.619	0.346	882.77	2.139	2.423	-1.32		
0.741	0.057	0.140	0.062	0.871	0.064	0.060	0.005	859.29	1.199	1.395	-2.55	0.019	0.017	0.590	0.374	886.67	2.205	2.486	-1.20		
0.742	0.057	0.138	0.062	0.873	0.062	0.059	0.005	859.23	1.182	1.375	-2.54	0.021	0.018	0.587	0.374	887.04	2.156	2.430	-1.21		
0.774	0.059	0.115	0.052	0.873	0.065	0.057	0.005	859.56	1.181	1.373	-2.57	0.016	0.016	0.565	0.403	891.99	2.202	2.469	-1.15		
0.774	0.059	0.115	0.052	0.866	0.064	0.064	0.006	859.55	1.193	1.388	-2.57	0.021	0.017	0.559	0.404	891.93	2.225	2.494	-1.13		
0.772	0.059	0.117	0.053	0.870	0.064	0.059	0.006	859.46	1.198	1.393	-2.52	0.016	0.015	0.565	0.404	891.09	2.220	2.491	-1.11		
0.426 ± 0.005	0.312	0.023	0.382	0.283	0.917	0.047	0.032	0.004	857.11	1.145	1.336	-2.12	0.009	0.011	0.558	0.422	893.15	2.164	2.423	-1.05	1.90
	0.306	0.026	0.383	0.284	0.913	0.056	0.028	0.003	857.40	1.188	1.385	-2.11	0.007	0.011	0.563	0.419	893.34	2.159	2.417	-1.09	1.97
	0.310	0.026	0.381	0.283	0.905	0.056	0.035	0.004	857.32	1.173	1.368	-2.14	0.007	0.011	0.561	0.420	893.97	2.174	2.432	-1.10	1.96

$w_{4,S}^b$	Overall Composition (OC)				Terpene-rich Phase (TP)								Solvent-rich Phase (SP)								$\pi$
	$w_1$	$w_2$	$w_3$	$w_4$	$w_1$	$w_2$	$w_3$	$w_4$	$\rho$	$\eta$	$\nu$	$V^E$	$w_1$	$w_2$	$w_3$	$w_4$	$\rho$	$\eta$	$\nu$	$V^E$	
	0.370	0.028	0.354	0.249	0.897	0.055	0.044	0.004	857.72	1.162	1.355	-2.28	0.010	0.010	0.561	0.419	894.05	2.177	2.435	-1.11	1.83
	0.372	0.028	0.350	0.250	0.897	0.054	0.045	0.004	857.67	1.152	1.343	-2.28	0.010	0.010	0.559	0.420	894.07	2.176	2.434	-1.10	1.75
	0.467	0.036	0.293	0.205	0.892	0.058	0.046	0.004	858.41	1.162	1.354	-2.39	0.011	0.011	0.557	0.421	896.04	2.198	2.453	-1.16	1.71
	0.463	0.036	0.288	0.214	0.910	0.060	0.027	0.004	858.37	1.156	1.346	-2.23	0.011	0.011	0.552	0.426	895.93	2.193	2.448	-1.11	1.76
	0.458	0.035	0.293	0.213	0.903	0.059	0.034	0.004	858.50	1.193	1.389	-2.31	0.010	0.012	0.557	0.422	896.20	2.193	2.447	-1.16	1.60
	0.555	0.042	0.237	0.166	0.888	0.061	0.048	0.004	858.93	1.166	1.357	-2.47	0.009	0.011	0.549	0.430	898.62	2.218	2.468	-1.17	1.57
	0.558	0.043	0.229	0.170	0.896	0.061	0.040	0.004	859.21	1.197	1.393	-2.46	0.010	0.013	0.539	0.438	899.09	2.230	2.480	-1.11	1.60
	0.532	0.041	0.243	0.183	0.903	0.062	0.031	0.004	858.96	1.187	1.382	-2.35	0.010	0.013	0.539	0.438	898.25	2.226	2.478	-1.08	1.55
	0.620	0.047	0.194	0.139	0.886	0.063	0.047	0.004	859.46	1.176	1.369	-2.54	0.009	0.011	0.535	0.445	901.36	2.233	2.477	-1.14	1.54
	0.620	0.047	0.193	0.140	0.900	0.063	0.033	0.004	859.58	1.178	1.371	-2.47	0.009	0.012	0.540	0.439	901.28	2.237	2.482	-1.19	1.57
	0.621	0.047	0.190	0.141	0.903	0.063	0.029	0.004	862.87	1.191	1.380	-2.99	0.007	0.013	0.541	0.439	902.02	2.242	2.485	-1.21	1.50
	0.614	0.047	0.195	0.144	0.902	0.063	0.031	0.004	859.59	1.200	1.396	-2.43	0.009	0.014	0.519	0.459	901.68	2.240	2.485	-1.02	
	0.696	0.053	0.149	0.101	0.885	0.065	0.046	0.004	860.18	1.185	1.377	-2.65	0.007	0.010	0.521	0.461	906.00	2.290	2.527	-1.16	1.35
	0.693	0.053	0.146	0.109	0.896	0.065	0.035	0.004	859.97	1.185	1.378	-2.54	0.005	0.012	0.517	0.466	906.25	2.169	2.393	-1.13	1.34
	0.675	0.051	0.158	0.115	0.885	0.064	0.046	0.005	859.98	1.194	1.388	-2.59	0.007	0.011	0.520	0.462	905.71	2.300	2.540	-1.14	1.40
0.508 ± 0.002	0.465	0.035	0.248	0.252	0.900	0.062	0.034	0.004	859.71	1.172	1.363	-2.51	0.004	0.006	0.476	0.514	914.31	2.279	2.493	-1.02	1.67
	0.468	0.036	0.246	0.250	0.909	0.064	0.023	0.004	859.79	1.204	1.401	-2.42	0.004	0.006	0.478	0.511	914.51	2.272	2.485	-1.04	1.68
	0.467	0.036	0.246	0.251	0.906	0.064	0.027	0.003	859.98	1.202	1.398	-2.51	0.002	0.006	0.472	0.519	914.57	2.272	2.484	-0.99	1.67
	0.620	0.047	0.165	0.168	0.899	0.066	0.031	0.004	860.61	1.185	1.376	-2.59	0.002	0.006	0.458	0.534	918.90	2.299	2.502	-1.01	1.37
	0.620	0.047	0.161	0.171	0.908	0.067	0.021	0.004	860.68	1.202	1.396	-2.53	0.003	0.007	0.460	0.530	919.36	2.303	2.505	-1.04	1.40
	0.614	0.047	0.165	0.175	0.901	0.065	0.030	0.004	860.74	1.209	1.405	-2.65	0.002	0.006	0.455	0.536	918.94	2.283	2.484	-0.99	1.38
	0.696	0.053	0.124	0.127	0.903	0.068	0.025	0.004	861.20	1.213	1.408	-2.66	0.003	0.005	0.457	0.536	924.07	2.301	2.491	-1.15	1.26
	0.697	0.053	0.121	0.129	0.901	0.067	0.029	0.003	861.26	1.212	1.408	-2.72	0.002	0.005	0.437	0.557	923.96	2.298	2.487	-0.98	1.29

<sup>a</sup> Standard uncertainties  $u$  are  $u(T) = 0.1$  K,  $u(p) = 1 \times 10^3$  Pa,  $u(w) \leq 0.001$ ,  $u(\rho) = 0.01$  kg·m<sup>-3</sup>,  $u(\eta) \leq 0.07$  mPa·s,  $u(\nu) \leq 0.07$  mm<sup>2</sup>·s<sup>-1</sup>, and  $u(\pi) \leq 0.01$  mN·m<sup>-1</sup>;

<sup>b</sup> Water mass fraction in the solvent, followed by the standard uncertainty.

The physical properties of the model and real orange systems were similar, confirming that the crude orange EO can be assumed to be a simple mixture of limonene and linalool. However, the interfacial tensions of the model and real acid lime systems were quite different, where the values of the model system were much higher than those of the real system. Some slight discrepancies can also be observed in density and viscosity values. These differences may be related to the complexity of the crude acid lime EO and the presence of other components in the real system, such as waxes, pigments, acids, and so forth. For comparison purposes, the interfacial tension between the crude EO and pure water were measured. The interfacial tension of the orange system varied from 7.42 to 10.2  $\text{mN}\cdot\text{m}^{-1}$ , while that of the acid lime system varied from 1.97 to 3.57  $\text{mN}\cdot\text{m}^{-1}$ . Since the citrus EOs used for the experimental assays of real systems were crude, non-volatile compounds such as waxes were present in the mixture (composition not determined). It was visually observed that lower interfacial tensions were probably related to higher non-volatile content in the aqueous phase (possibly waxes). Moreover, it was also visually observed that the solvent phases from the acid lime systems had a higher “wax” volume than those of the orange systems. These observations may explain the low interfacial tension values of the acid lime real system.

#### VI.3.2.1. Correlated and calculated data

**Density:** Table 7 contains the relative deviations for the estimated densities of the LLE phases by the simple mixing rule [Eq. (4)] for compositions in either mass fraction or molar fraction. For the terpene-rich phases (TP in table), better results were calculated using the compositions in molar fraction ( $\Delta = 0.10 - 1.68\%$ ), while for the solvent-rich phases (SP in table), the deviations were lower using the compositions in mass fraction ( $\Delta = 1.53 - 2.36\%$ ). The same tendency was observed by Gonçalves et al. [10] for a eucalyptus model system. A good estimation of densities by the simple mixing rule can be confirmed by low excess volumes values ( $V^E$ ) [10] calculated by Eq. (5) and shown in Tables 3 – 6.

Relating to excess volume values, we can verify that they were positive for terpene-rich phases (with the exception of the acid lime real system, Table 6) and always negative for the solvent-rich phases. The breaking of cohesion forces and unfavorable interactions between distinct molecules are responsible for positive  $V^E$  values, while the negative values are related to interactions among unlike molecules (e.g., terpenes and water) by charge–transfer and dipole–dipole interactions among the solvent molecules (ethanol and water) [24]. Furthermore, excess volumes of the terpene-rich phases from the model (Table 3) and real (Table 5) orange systems were very low ( $0.25 - 0.58 \text{ cm}^3\cdot\text{mol}^{-1}$ ), implying a high proximity to an ideal mixture.

**Table 7:** Average relative deviations ( $\Delta$ ), in %, between the experimental and calculated physical property values.

%w water in the solvent	Density $\Delta(\rho)$				Dynamic Viscosity $\Delta(\eta)$				Kinematic Viscosity $\Delta(\nu)$						Interfacial Tension $\Delta(\pi)$	
	Simple Mixture Rule, in $w$		Simple Mixture Rule, in $x$		Grunberg– Nissan, in $w$		Grunberg– Nissan, in $x$		Grunberg– Nissan, in $w$		Grunberg– Nissan, in $x$		UNIFAC– VISCO		Linear Adjustment in $w$	Linear Adjustment in $x$
	TP <sup>a</sup>	SP <sup>b</sup>	TP <sup>a</sup>	SP <sup>b</sup>	TP <sup>a</sup>	SP <sup>b</sup>	TP <sup>a</sup>	SP <sup>b</sup>	TP <sup>a</sup>	SP <sup>b</sup>	TP <sup>a</sup>	SP <sup>b</sup>	TP <sup>a</sup>	SP <sup>b</sup>		
<b>Orange Essential Oil Model System</b>																
23%	0.38	1.21	0.27	3.78	2.30	1.35	2.51	4.92	2.25	1.37	2.67	5.41	28.6	12.4	1.97	8.8
30%	0.34	1.50	0.30	3.94	3.63	2.18	4.06	3.17	3.56	2.43	4.31	3.66	22.0	4.10	2.49	11.5
40%	0.34	1.85	0.31	3.62	4.60	2.13	7.54	7.77	4.37	0.96	7.53	6.85	26.3	3.20	3.38	11.8
$\Delta(\%)^c$	0.36	1.53	0.29	3.79	3.56	1.91	4.87	5.28	<b>3.44</b>	<b>1.60</b>	5.02	5.27	25.5	5.86	<b>2.67</b>	10.3
<b>Orange Essential Oil Real System</b>																
30%	0.27	2.45	0.13	3.30	6.31	3.12	2.14	2.78	6.16	1.67	2.03	2.89	17.2	1.92	5.68	1.95
40%	0.24	2.24	0.15	3.09	0.98	3.56	7.18	1.93	0.91	5.58	7.65	12.4	20.9	2.31	13.4	6.46
$\Delta(\%)^c$	0.26	2.36	0.14	3.21	4.06	3.30	4.27	2.42	<b>3.94</b>	3.32	4.41	6.91	18.8	<b>2.08</b>	9.15	<b>3.98</b>
<b>Lemon/Lime Essential Oil Model System</b>																
30%	5.66	1.79	0.10	3.62	2.38	2.93	7.10	10.2	2.34	3.09	5.23	8.86	41.9	2.38	7.50	13.0
40%	4.26	2.10	0.11	3.35	2.07	2.48	3.66	8.44	2.09	2.31	2.59	6.38	38.2	2.44	6.07	8.75
50%	2.89	2.01	0.09	3.00	2.33	1.81	5.83	10.6	2.19	1.83	3.62	12.7	36.4	2.40	3.75	7.38
$\Delta(\%)^c$	4.25	1.97	0.10	3.32	2.26	2.40	5.50	9.75	<b>2.21</b>	<b>2.40</b>	3.78	9.33	38.8	2.41	<b>5.74</b>	9.66
<b>Acid Lime Essential Oil Real System</b>																
20%	1.27	1.80	1.65	2.77	3.37	8.49	6.85	22.8	1.92	8.25	14.0	16.8	34.3	13.6	41.9	31.3
24%	1.39	2.02	1.50	3.01	4.08	4.02	8.46	28.0	2.56	3.69	19.8	15.0	31.5	11.1	11.9	20.5
30%	1.57	2.09	1.77	3.37	6.57	2.30	16.5	8.37	5.24	2.35	15.7	5.46	27.8	4.34	32.8	30.6
40%	1.58	2.18	1.67	3.18	6.52	6.50	11.9	6.76	5.72	6.50	11.0	11.4	19.9	1.15	106	97.8
50%	1.67	2.23	1.63	2.66	7.43	3.28	12.7	20.1	6.59	3.34	11.8	23.5	15.9	3.78	194	170
$\Delta(\%)^c$	1.54	2.10	1.68	3.11	6.08	4.56	12.7	13.0	<b>4.95</b>	<b>4.53</b>	14.0	11.9	24.8	4.93	90.8	82.4
$\Delta(\text{global})^d$	1.60	<b>1.99</b>	<b>0.55</b>	3.36									27.8	5.02		

<sup>a</sup> Terpene-rich phase;

<sup>b</sup> Solvent-rich phase;

<sup>c</sup> Average relative deviation for the phase (for density and viscosity) or system (for interfacial tension);

<sup>d</sup> Global relative deviation of the prediction procedure.

**Viscosity:** The parameters of the Grunberg–Nissan model adjusted for the model systems for both dynamic and kinematic viscosities, using the compositions in mass and molar fractions, are shown in Table 8. The relative deviations between the calculated and experimental values are exposed in Table 7. For the orange model system, better adjustments were reached for kinematic viscosity ( $\nu$ ) for both terpene-rich ( $\Delta = 3.44\%$ ) and solvent-rich phases ( $\Delta = 1.60\%$ ), using the compositions in mass fraction ( $w$ ). The adjusted Grunberg–Nissan parameters provided satisfactory results on the prediction of the phase kinematic viscosity values from the orange real systems using the composition in mass fraction ( $\Delta = 3.94\%$  for the terpene-rich phase, and  $\Delta = 3.32\%$  for the solvent-rich phase).

**Table 8:** Grunberg–Nissan parameters for model systems at  $T = 298.2 \pm 0.1$  K.

Parameter	Dynamic Viscosity ( $\eta$ )		Kinematic Viscosity ( $\nu$ )	
	$w^a$	$x^b$	$w^a$	$x^b$
Orange Essential Oil Model System				
G <sub>12</sub>	-1.86	28.2	-1.84	28.4
G <sub>13</sub>	-8.4	2.47	-8.15	2.44
G <sub>14</sub>	31.9	-27.5	31.2	-27.1
G <sub>23</sub>	-1.05	-268	-1.13	-271
G <sub>24</sub>	4.89	271	5.04	274
G <sub>34</sub>	6.1	6.32	5.93	6.6
Lemon/Lime Essential Oil Model System				
G <sub>12</sub>	-71.8	-32	-70.1	-31
G <sub>13</sub>	160	187	150	183
G <sub>14</sub>	73.5	1548	81.4	1558
G <sub>15</sub>	307	-32	313	-35
G <sub>16</sub>	-804	-6211	-833	-6234
G <sub>23</sub>	27.5	-16	28.2	-17
G <sub>24</sub>	-12.7	-6	-13.7	-7
G <sub>25</sub>	143	262	135	261
G <sub>26</sub>	-233	-1166	-216	-1164
G <sub>34</sub>	-9.3	-1331	-12.5	-1335
G <sub>35</sub>	-843	-1005	-817	-999
G <sub>36</sub>	1478	10233	1426	10246
G <sub>45</sub>	1.6	-41	2.5	-41
G <sub>46</sub>	17.5	-6	16.4	-4
G <sub>56</sub>	7.4	9	7.2	9
Lemon/Lime Essential Oil Model System (used for the Real System)				
G <sub>12</sub>	1.12	8.05	1.1	7.97
G <sub>13</sub>	-0.26	1.26	-0.4	1.09
G <sub>14</sub>	-16.9	-12.9	-17.7	-12.6
G <sub>23</sub>	6.93	-25.9	8.18	-25.4
G <sub>24</sub>	7.21	-83.8	5.36	-83
G <sub>34</sub>	7.29	8.21	7.07	8.44

<sup>a</sup> Phases composition in mass fraction;

<sup>b</sup> Phases composition in molar fraction.

Relating to the acid lime model systems, both dynamic and kinematic viscosities exhibited a good adjustment ( $\Delta = 2.21 - 2.40\%$ ) using the Grunberg–Nissan model and the phase composition in mass fraction. For the acid lime real system, better predicted values were calculated using the Grunberg–Nissan parameters for kinematic viscosity and the phases compositions in mass fraction ( $\Delta = 4.53\%$  for the solvent-rich phase, and  $\Delta = 4.95\%$  for the terpene-rich phase).

The kinematic viscosity values predicted by the UNIFAC–VISCO model presented good results for the solvent-rich phases ( $\Delta = 5.02\%$ ) but was not efficient for the terpene-rich phases ( $\Delta = 27.8\%$ ).

**Interfacial Tension:** The linear adjustment for the interfacial tensions of the orange model system is shown in Eq. (10) for mass fraction and in Eq. (11) for molar fraction. The adjustment of the lemon/lime model system is shown in Eq. (12) for mass fraction and in Eq. (13) for molar fraction. We can verify that adjustments were better using the compositions in mass fraction (higher  $R^2$  values).

$$\pi = -1.1093 - 1.4768 \times \ln(w_{limonene,SP} + w_{linalool,SP} + w_{ethanol,TP} + w_{water,TP}) \quad R^2 = 0.8511 \quad (10)$$

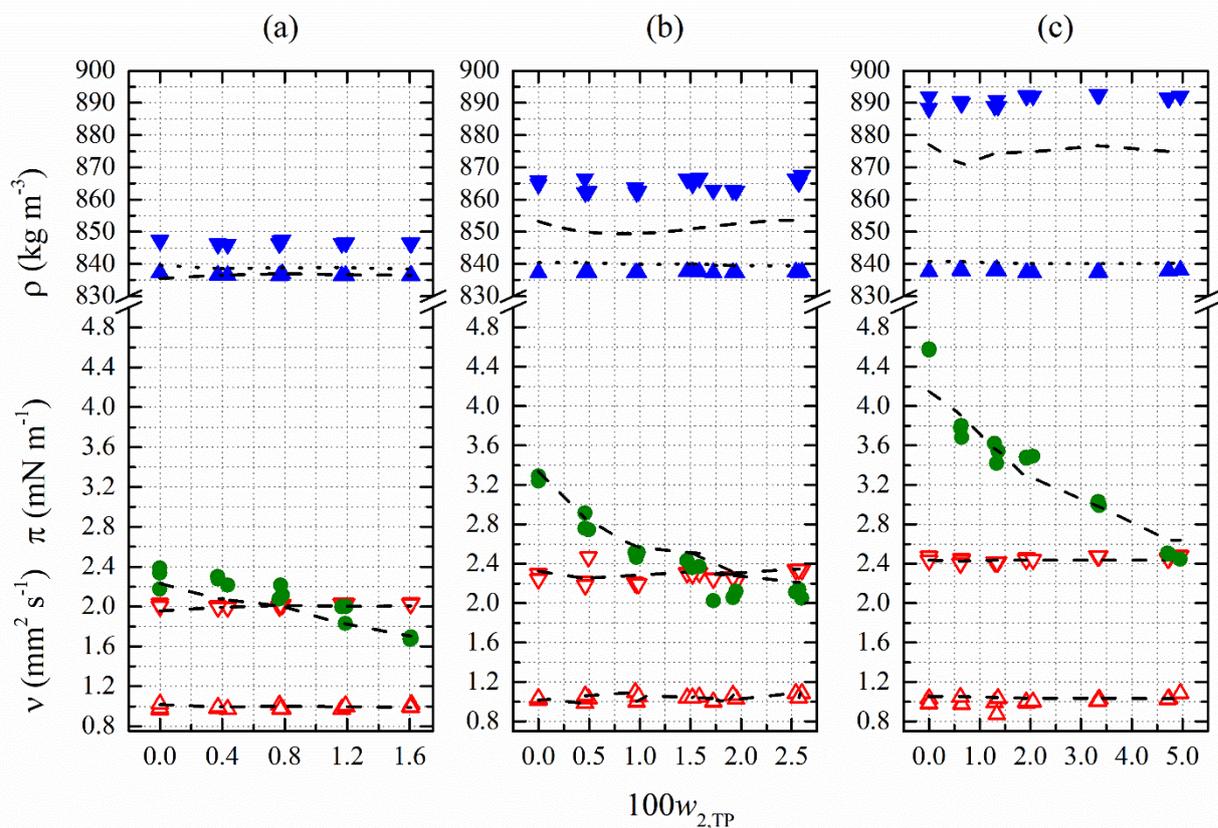
$$\pi = -2.0889 - 2.1747 \times \ln(x_{limonene,SP} + x_{linalool,SP} + x_{ethanol,TP} + x_{water,TP}) \quad R^2 = 0.7526 \quad (11)$$

$$\pi = -2.2514 - 2.1008 \times \ln(w_{terpenes,SP} + w_{citral,SP} + w_{ethanol,TP} + w_{water,TP}) \quad R^2 = 0.9445 \quad (12)$$

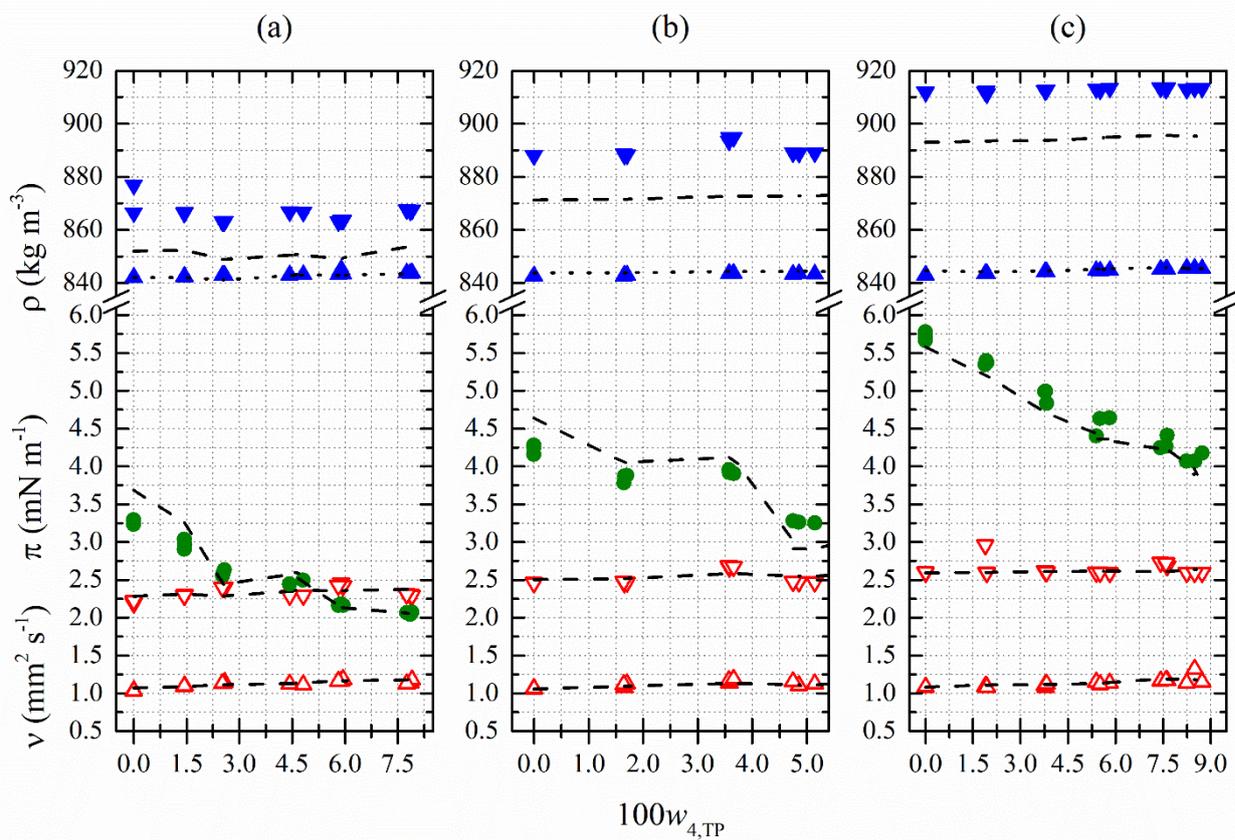
$$\pi = -2.6536 - 2.9132 \times \ln(x_{terpenes,SP} + x_{citral,SP} + x_{ethanol,TP} + x_{water,TP}) \quad R^2 = 0.8369 \quad (13)$$

The parameters adjusted to the model system were used to predict the interfacial tension values of the real systems. The deviations for the adjustment and the prediction are shown in Table 7, where it is possible to observe that for the orange real system, the approach using the composition in molar fraction [Eq. (11)] provided better results ( $\Delta = 3.98\%$ ). For the acid lime real systems, both Eqs. (12) and (13) were not effective in the calculation of the interfacial tensions. This property is much more complex than the others, since several factors affect its value, such as the solubility of the phases and the differences between the densities and viscosities of the phases. Moreover, differences between the experimental interfacial tensions of the model and the real systems were observed, which may be related to the wax present in the system, as discussed in section 3.2.

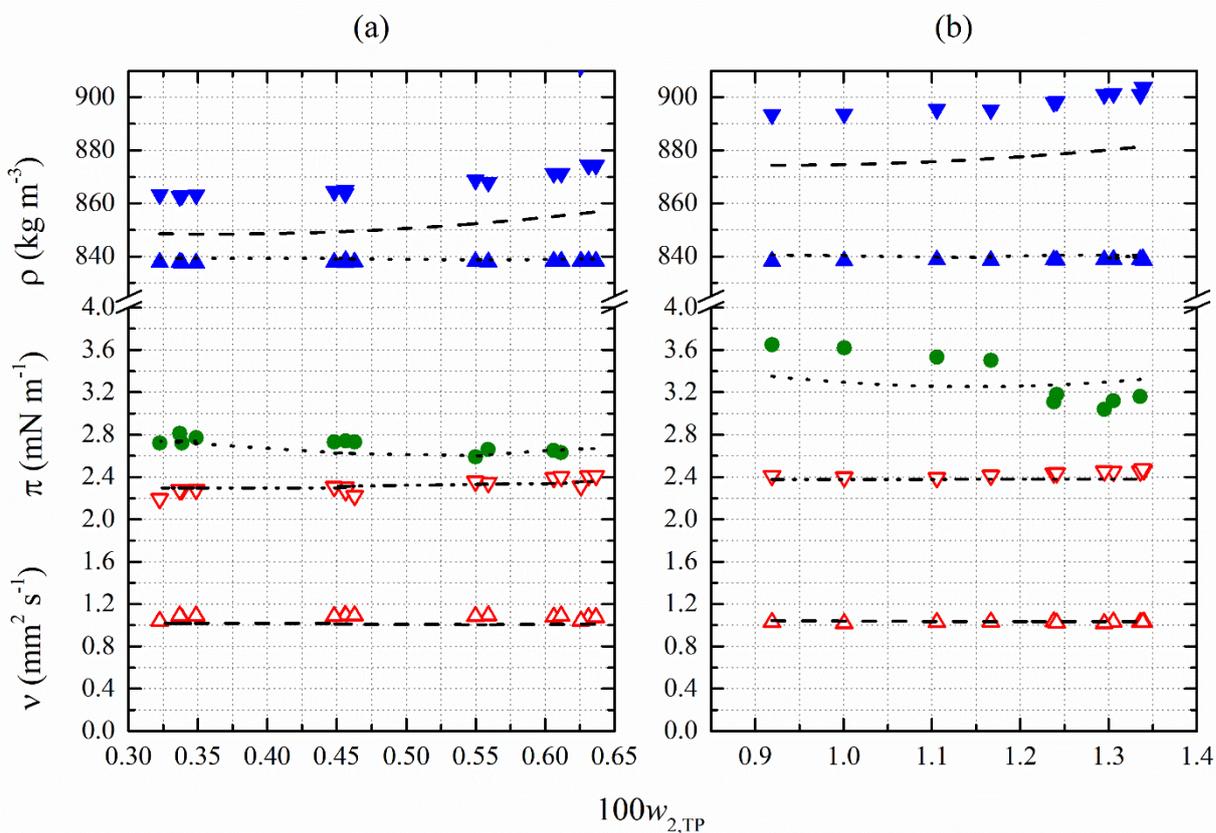
The experimental physical properties and the improved results of their respective correlated or predicted values, according to the highlighted deviations in Table 7, are displayed in Fig. 1 and Fig. 2 for orange and lemon/lime model systems, respectively, and in Fig. 3 and Fig. 4 for orange and acid lime real systems, respectively. The predicted interfacial tension values of the acid lime real systems were not exhibited in Fig. 4.



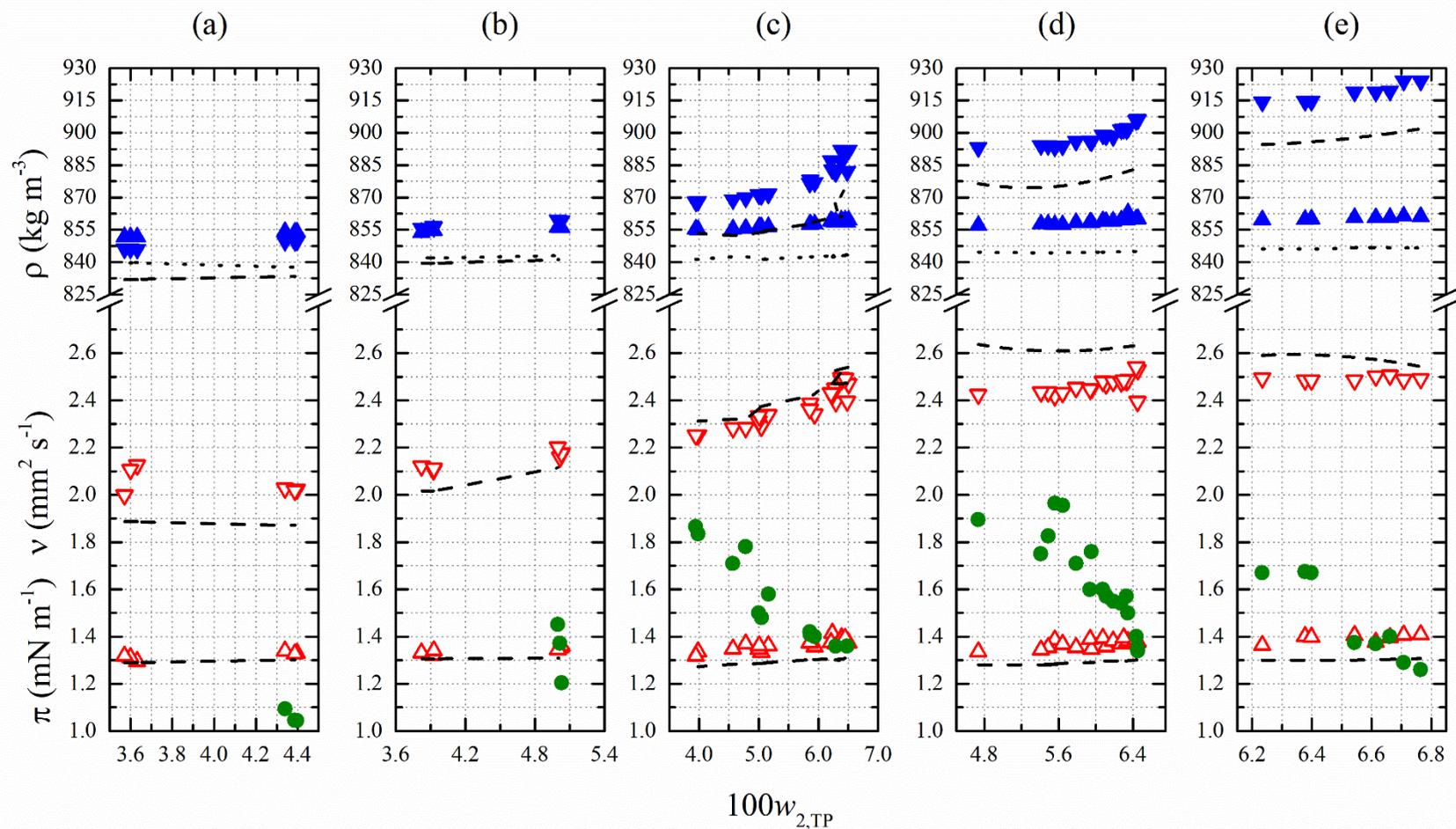
**Fig. 1** - Physical properties of the phases from the liquid–liquid equilibrium of the orange model system with respect to the mass percentage of linalool in the terpene-rich phase ( $100w_{2,TP}$ ) at  $298.2 \pm 0.1$  K. Experimental values:  $\triangle/\nabla$ , kinematic viscosity ( $\nu$ , in  $\text{mm}^2 \cdot \text{s}^{-1}$ );  $\triangle/\nabla$ , density ( $\rho$ , in  $\text{kg} \cdot \text{m}^{-3}$ );  $\bullet$ , interfacial tension ( $\pi$ , in  $\text{mN} \cdot \text{m}^{-1}$ ).  $\triangle/\triangle$ , terpene-rich phases;  $\nabla/\nabla$ , solvent-rich phases. Calculated values:  $\cdots$ , approach with molar fraction ( $x$ );  $---$ , approach with mass fraction ( $w$ ). Water mass fraction in the solvent: (a)  $0.235 \pm 0.002$ , (b)  $0.311 \pm 0.003$ , and (c)  $0.426 \pm 0.005$ .



**Fig. 2** - Physical properties of the phases from the liquid-liquid equilibrium of the lemon/lime model system with respect to the mass percentage of citral in the terpene-rich phase ( $100w_{4,TP}$ ) at  $298.2 \pm 0.1$  K. Experimental values:  $\triangle/\nabla$ , kinematic viscosity ( $\nu$ , in  $\text{mm}^2 \cdot \text{s}^{-1}$ );  $\triangle/\nabla$ , density ( $\rho$ , in  $\text{kg} \cdot \text{m}^{-3}$ );  $\bullet$ , interfacial tension ( $\pi$ , in  $\text{mN} \cdot \text{m}^{-1}$ ).  $\triangle/\triangle$ , terpene-rich phases;  $\nabla/\nabla$ , solvent-rich phases. Calculated values:  $\cdots$ , approach with molar fraction ( $x$ );  $- -$ , approach with mass fraction ( $w$ ). Water mass fraction in the solvent: (a)  $0.311 \pm 0.003$ , (b)  $0.426 \pm 0.005$ , and (c)  $0.508 \pm 0.002$ .



**Fig. 3** - Physical properties of the phases from the liquid–liquid equilibrium of the orange real system with respect to the mass percentage of oxygenated compounds in the terpene-rich phase ( $100w_{2,TP}$ ) at  $298.2 \pm 0.1$  K. Experimental values:  $\Delta/\nabla$ , kinematic viscosity ( $v$ , in  $\text{mm}^2\cdot\text{s}^{-1}$ );  $\blacktriangle/\blacktriangledown$ , density ( $\rho$ , in  $\text{kg}\cdot\text{m}^{-3}$ );  $\bullet$ , interfacial tension ( $\pi$ , in  $\text{mN}\cdot\text{m}^{-1}$ ).  $\Delta/\blacktriangle$ , terpene-rich phases;  $\nabla/\blacktriangledown$ , solvent-rich phases. Calculated values:  $\cdots$ , approach with molar fraction ( $x$ );  $- - -$ , approach with mass fraction ( $w$ );  $\cdots-$ , UNIFAC–VISCO model. Water mass fraction in the solvent: (a)  $0.311 \pm 0.003$ , (b)  $0.426 \pm 0.005$ , and (c)  $0.508 \pm 0.002$ .



**Fig. 4** - Physical properties of the phases from the liquid-liquid equilibrium of the acid lime real system with respect to the mass percentage of oxygenated compounds in the terpene-rich phase ( $100w_{2,TP}$ ) at  $298.2 \pm 0.1$  K. Experimental values:  $\triangle/\nabla$ , kinematic viscosity ( $\nu$ , in  $\text{mm}^2 \cdot \text{s}^{-1}$ );  $\blacktriangle/\blacktriangledown$ , density ( $\rho$ , in  $\text{kg} \cdot \text{m}^{-3}$ );  $\bullet$ , interfacial tension ( $\pi$ , in  $\text{mN} \cdot \text{m}^{-1}$ ).  $\triangle/\blacktriangle$ , terpene-rich phases;  $\nabla/\blacktriangledown$ , solvent-rich phases. Calculated values:  $\cdots$ , approach with molar fraction ( $x$ );  $- -$ , approach with mass fraction ( $w$ ). Water mass fraction in the solvent: (a)  $0.206 \pm 0.008$ , (b)  $0.247 \pm 0.001$ , (c)  $0.311 \pm 0.003$ , (d)  $0.426 \pm 0.005$ , and (e)  $0.508 \pm 0.002$ .

#### **VI.4. Conclusions**

In general, increasing the water content in the solvent led to higher values of density, dynamic viscosity, surface tension, and interfacial tension. Increasing the amount of oxygenated compounds also resulted in higher values of density and dynamic viscosity but attenuated interfacial tension.

The GCVOL model provided suitable performance in the estimation of density values of the pure components. The simple mixing rule was also efficient in the estimation of density values of the phases from the liquid–liquid equilibrium.

The parameters of the Grunberg–Nissan, adjusted for the model systems, exhibited satisfactory results on the calculation of viscosity values of the phases. The parameters of the UNIFAC–VISCO model provided good results in the calculation of viscosity of the extracted phases.

The linear equation adjusted for the orange model system presented a good description of the interfacial tensions of the real systems. However, the same was not observed for the acid lime real systems.

Overall, it is possible to observe that empirical models can easily be applied to the estimation of values of important physical properties of the phases from the systems evaluated in this study.

#### **VI. Acknowledgments**

We would like to acknowledge FAPESP (Fundação de Amparo à Pesquisa do Estado de São Paulo, 13/11150-3, 14/22272-5), CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico, 303797/2016-9, 308615/2016-6), FINEP (Inovação e Pesquisa, 01/11/0140/00), CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior) for the financial support, and Louis Dreyfus Company (Mr. Antonio Carlos Gonçalves) for the crude orange and acid lime essentials oil donation.

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#### 4. GENERAL CONCLUSIONS

The key findings of this research were:

- The fractionation of citrus essential oils using ethanol and water as solvents was possible, and extract/ solvent phases, rich in oxygenated compounds, were obtained;
- Fractionating of citrus essential oils using the continuous equipment (PRDC) provided satisfactory performance, and may be an alternative for industrial processes;
- Increased water content in the solvent led to:
  - lower solubility of the phases, denoting to lower migration of terpenes and oxygenated compounds to the extract phases (lower values of partition coefficients and extraction indices);
  - higher solvent selectivity for the oxygenated compounds;
  - higher density and viscosity values, mainly of the extract phases (solvent-rich phases);
  - higher interfacial tension values;
  - higher folding values (PRDC assays);
  - higher mass transfer units (PRDC assays);
  - faster separation of the phases in the PDRC equipment;
  - lower volumetric overall mass transfer coefficient values (PRDC assays);
  - lower migration of solvent to the raffinate phase;
  - higher differences between the densities of raffinate and extract phases;
  - higher differences between the viscosities of raffinate and extract phases;
- Increased oxygenated compounds content in the mixtures led to:
  - higher solubility of the phases, denoting to higher migration of terpenes and oxygenated compounds to the extract phases (higher values of partition coefficients and extraction indices);
  - lower solvent selectivity for the oxygenated compounds;
  - higher density and viscosity values;
  - lower interfacial tension values;
  - lower folding values (PRDC assays);

- higher volumetric overall mass transfer coefficient values (PRDC assays);
- slower separation of the phases in the PDRC equipment;
- higher differences between the densities of raffinate and extract phases;
- higher differences between the viscosities of raffinate and extract phases;
- Calculated data:
  - The binary interaction parameters of the NRTL and UNIQUAC thermodynamic models adjusted for the model systems (limonene + linalool + ethanol + water) were effective on the calculation of the compositions of the phases from the real systems (crude orange essential oil + ethanol + water), at 298.2 K;
  - The binary interaction parameters of the NRTL thermodynamic model, from the literature, adjusted for the model systems (limonene  $\beta$ -pinene +  $\gamma$ -terpinene + linalool + ethanol + water) were efficient on the calculation of the compositions of the phases from the real systems (crude acid lime oil + ethanol + water), at 298.2 K;
  - The simple mixing rule provided satisfactory results on the estimation of density values of both terpenic and solvent phases;
  - The binary parameters of the Grunberg–Nissan model, adjusted for the model systems, were suitable on the calculation of the viscosity values of the phases from the real systems;
  - The parameters of UNIFAC–VISCO model were efficient on the calculation of the kinematic viscosity values of the solvent phases;
  - The linear parameters adjusted for the interfacial tension of the orange model systems were satisfactory on the calculation of the interfacial tension values of the real systems;
- Aroma profile:
  - The increase on the water content in the solvent did not affect strongly the aroma profile of the phases from the liquid–liquid equilibrium;
  - The phases from the liquid–liquid equilibrium exhibited aroma profile similar to the ones of the crude essential oils;
  - For the orange essential oil:
    - the main components responsible for the typical aroma were  $\alpha$ -pinene > limonene > octanal > linalool > citronellal > nonanal;

- the crude essential oil and the phases from the liquid–liquid equilibrium were classified as citrus and herbaceous scent, with woody, floral, green, and fruity *nuances*.
- For the acid lime essential oil:
  - the main components responsible for the typical aroma were  $\alpha$ -pinene > limonene > neral = geranial >  $\gamma$ -terpinene >  $\beta$ -pinene = geraniol > linalool > decanal >  $\alpha$ -terpineol;
  - the crude essential oil and the phases from the liquid–liquid equilibrium were classified as herbaceous and citrus scent with floral, woody, and oriental *nuances*.

## 5. SUGGESTIONS FOR FUTURE STUDIES

Although the fractionation process of citrus essential oils was deeply studied during the master's and doctorate degrees, some studies still may be proposed:

- Evaluation of the non-volatile compounds present in the crude essential oils and their effect over the liquid–liquid equilibrium data, mainly over the physical properties of the phases;
- Evaluation of the surface tension of the phases from the liquid–liquid equilibrium;
- Determination of the interfacial tensions using citrus essential oils without wax, mainly the acid lime essential oil;
- Determination of the interfacial tensions of systems composed of bergamot essential oil + ethanol + water;
- Adjustment of parameters of other models to calculate the interfacial tension values of real systems;
- Use of different versions of the UNIFAC model to describe the vapor–liquid equilibrium;
- Evaluation of the aroma profile of systems composed of other citrus essential oils, such as bergamot or grapefruit;
- Determination of the maximum water content in the solvent that changes expressively the aroma profile of the phases from the liquid–liquid equilibrium;
- Evaluation of the fractionation process performance in PRDC by computational simulation, using the software Aspen Plus®;
- Correlation of the liquid–liquid equilibrium data with other thermodynamic properties, such as the polarity of the components, for instance;
- Development of a beverage or perfume using the extract phases from the fractionation process;
- Estimation of the economic viability of the fractionation process using the PRDC and comparison with the conventional distillation or vacuum distillation.

“Somewhere, something incredible is waiting to be known”

Carl Sagan

## 6. POSTGRADUATE MEMORY

### 6.1. Timeline

2011 – 2013: Master's Degree, FZEA/USP, Brazil.

2013 – 2015: Doctorate course, FZEA/USP, Brazil.

2015 – 2016: Exchange internship, FEUP, Portugal.

2016 – 2017: Doctorate Degree, FZEA/USP, Brazil.

### 6.2. Scientific articles published

- 1) **Daniel Gonçalves**, Cristina C. Koshima, Karina T. Nakamoto, Tayla K. Umeda, Keila K. Aracava, Cintia B. Gonçalves, Chriatianne E. da C. Rodrigues, Deterpenation of eucalyptus essential oil by liquid+liquid extraction: Phase equilibrium and physical properties for model systems at T=298.2K, *The Journal of Chemical Thermodynamics*, 69 (2014) 66–72. doi:10.1016/j.jct.2013.09.044.
- 2) **Daniel Gonçalves**, Martin E.E. Teschke, Cristina C. Koshima, Cintia B. Gonçalves, Alessandra L. Oliveira, Christianne E.C. Rodrigues, Fractionation of orange essential oil using liquid–liquid extraction: Equilibrium data for model and real systems at 298.2 K, *Fluid Phase Equilibria*, 399 (2015) 87–97. doi:10.1016/j.fluid.2015.04.022.
- 3) **Daniel Gonçalves**, Martin E.E. Teschke, Cristina C. Koshima, Chritianne E.C. Rodrigues, Fractionation of citrus essential oil by liquid–liquid extraction using a perforated rotating disc contactor, *Separation and Purification Technology*, 163 (2016) 247–257. doi:10.1016/j.seppur.2016.03.002.
- 4) **Daniel Gonçalves**, Patrícia Costa, Christianne E.C. Rodrigues, Alírio E. Rodrigues, Fractionation of acid lime essential oil using ethanol/water mixtures: Effect of the process on the aroma profile, *The Journal of Chemical Thermodynamics*, 108 (2017) 118–126. doi:10.1016/j.jct.2017.01.012.
- 5) **Daniel Gonçalves**, Patrícia Costa, Christianne E.C. Rodrigues, Alírio E. Rodrigues. Effect of Citrus sinensis essential oil deterpenation on the aroma profile of the phases obtained by solvent extraction. *The Journal of Chemical Thermodynamics*, accepted for publication.

### 6.3. Papers and abstracts published in scientific events

- 1) **Daniel Gonçalves**, Martin E.E. Teschke, Keila K. Aracava, Christianne E.C. Rodrigues. *Desterpenação de óleo essencial cítrico modelo por extração líquido–líquido (ELL)* (expanded abstract). *Annals of the I Simpósio de Pós-Graduação*, Pirassununga/SP, Brazil, 2012.
- 2) **Daniel Gonçalves**, Keila K. Aracava, Christianne E.C. Rodrigues. *Estudo do processo de desterpenação de sistema modelo limoneno-linalol por extração líquido–líquido* (abstract

- and paper). Annals of the XIX *Congresso Brasileiro de Engenharia Química* (COBEQ), Búzios/RJ, Brazil, 2012.
- 3) Tayla K. Umeda; Karina. T. Nakamoto, **Daniel Gonçalves**, Cristina C. Koshima, Keila K. Aracava, Christianne E.C. Rodrigues. *Equilíbrio de fases do sistema modelo limoneno, citronelal, etanol e água a 25 °C* (abstract). Annals of the XXIII *Congresso Brasileiro de Ciência e Tecnologia de Alimentos* (CBCTA), Campinas/SP, Brazil, 2013.
  - 4) **Daniel Gonçalves**, Martin E.E. Teschke, Cristina C. Koshima, Alessandra L. Oliveira, Christianne E.C. Rodrigues. *Equilíbrio de fases do sistema composto por óleo essencial cítrico, etanol e água a 25 °C* (abstract and paper). Annals of the VII *Congresso Brasileiro de Termodinâmica Aplicada*, Uberlândia/MG, Brazil, 2013.
  - 5) Martin E.E. Teschke, **Daniel Gonçalves**, Cristina C. Koshima, Christianne E.C. Rodrigues. *Equilíbrio de fases do sistema composto por óleo essencial de laranja, etanol e água a 25 °C* (expanded abstract). Annals of the 21° *Simpósio Internacional de Iniciação Científica da Universidade de São Paulo* (SIICUSP), Piracicaba/SP, Brazil, 2013.
  - 6) Mayara F. Paludetti, **Daniel Gonçalves**, Christianne E.C. Rodrigues. *Equilíbrio de fases do sistema composto por óleo essencial bruto de lima ácida, etanol e água, a 25 °C* (abstract and paper). Annals of the 22° *Simpósio Internacional de Iniciação Científica da Universidade de São Paulo* (SIICUSP), Pirassununga/SP, Brazil, 2014.
  - 7) Christianne E.C. Rodrigues, Cristina C. Koshima, **Daniel Gonçalves**. Behavior of terpenes, sesquiterpenes and oxygenated compounds during the essential oil deterpenation process by liquid–liquid extraction, at 298.2 K (expanded abstract). Annals of the 13<sup>th</sup> *Mediterranean Congress of Chemical Engineering*, Barcelona, Spain, 2014.
  - 8) **Daniel Gonçalves**, Mayara F. Paludetti, Cristina C. Koshima, Cintia B. Gonçalves, Christianne E.C. Rodrigues. *Dados de propriedades físicas de sistema modelo de óleo essencial cítrico composto por limoneno, linalol, etanol e água, a 25 °C* (abstract and paper). Annals of the XX *Congresso Brasileiro de Engenharia Química* (COBEQ), Florianópolis/SC, Brazil, 2014.
  - 9) **Daniel Gonçalves**, Martin E.E. Teschke, Christianne E.C. Rodrigues. *Fracionamento de óleo essencial cítrico modelo em equipamento contínuo: Análise de desempenho do processo* (abstract and paper). Annals of the XX *Congresso Brasileiro de Engenharia Química* (COBEQ), Florianópolis/SC, Brazil, 2014.
  - 10) **Daniel Gonçalves**, Cristina C. Koshima, Martin E.E. Teschke, Christianne E.C. Rodrigues. *Cálculos dos coeficientes de transferência de massa e número de estágios teóricos de equipamento contínuo aplicado ao fracionamento de óleo essencial cítrico* (abstract and paper). Annals of the XX *Congresso Brasileiro de Engenharia Química* (COBEQ), Florianópolis/SC, Brazil, 2014.
  - 11) Cristina C. Koshima, **Daniel Gonçalves**, Karina T. Nakamoto, Christianne E.C. Rodrigues. *Deterpenação por extração líquido-líquido de mistura modelo de óleo de bergamota em coluna PRDC* (abstract and paper). Annals of the XX *Congresso Brasileiro de Engenharia Química* (COBEQ), Florianópolis/SC, Brazil, 2014.

- 12) **Daniel Gonçalves**, Mayara F. Paludetti, Cintia B. Gonçalves, Christianne E.C. Rodrigues. Physical properties of systems composed of crude orange essential oil, ethanol and water at 25 °C (expanded abstract). *Annals of the International Conference on Chemical and Biochemical Engineering*, Paris, France, 2015.
- 13) Mayara F. Paludetti, **Daniel Gonçalves**, Christianne E.C. Rodrigues. *Determinação experimental de tensão interfacial de sistemas modelo compostos por limoneno, linalol, etanol e água, a 25 °C* (abstract). *Annals of the 11º Simpósio Latino Americano de Ciência de Alimentos (SLACA)*, Campinas/SP, Brazil, 2015.
- 14) Mayara F. Paludetti, **Daniel Gonçalves**, Christianne E.C. Rodrigues. *Determinação experimental de tensão interfacial de sistemas modelo compostos por  $\gamma$ -terpineno, limoneno,  $\beta$ -pineno, citral, etanol e água, a 25 °C* (abstract). *Annals of the 11º Simpósio Latino Americano de Ciência de Alimentos (SLACA)*, Campinas/SP, Brazil, 2015.
- 15) **Daniel Gonçalves**, Mayara F. Paludetti, Cintia B. Gonçalves, Christianne E.C. Rodrigues. *Fracionamento de óleos essenciais cítricos em coluna de discos rotativos perfurados utilizando misturas de etanol e água como solventes* (abstract and paper). *Annals of the XXI Congresso Brasileiro de Engenharia Química (COBEQ)*, Fortaleza/CE, Brazil, 2016.
- 16) **Daniel Gonçalves**, Mayara F. Paludetti, Cintia B. Gonçalves, Christianne E.C. Rodrigues. *Tensão interfacial de sistemas compostos por óleo essencial cítrico, etanol e água, a 25 °C* (abstract and paper). *Annals of the XXI Congresso Brasileiro de Engenharia Química (COBEQ)*, Fortaleza/CE, Brazil, 2016.

#### **6.4. Participation of the Teaching Improvement Program (*Programa de Aperfeiçoamento de Ensino - PAE*)**

- 1) *Operações Unitárias I* (Unit Operations I). Undergraduate subject of Food Engineering course (2<sup>st</sup> semester, 2011), FZEA/USP, Pirassununga/SP, Brazil. Responsible: Professor Dr. Cynthia Ditchfield.
- 2) *Planejamento e Projetos I* (Planning and Projects I). Undergraduate subject of Food Engineering course (1<sup>st</sup> semester, 2012), FZEA/USP, Pirassununga/SP, Brazil. Responsible: Professors Dr. Cynthia Ditchfield and Dr. Rogers Ribeiro.
- 3) *Fundamentos da Engenharia de Alimentos* (Food Engineering Fundamentals). Undergraduate subject of Food Engineering course (1<sup>st</sup> semester, 2014), FZEA/USP, Pirassununga/SP, Brazil. Responsible: Professor Dr. Cintia Bernardo Gonçalves.
- 4) *Operações Unitárias III* (Unit Operations III). Undergraduate subject of Food Engineering course (2<sup>st</sup> semester, 2014), FZEA/USP, Pirassununga/SP, Brazil. Responsible: Professor Dr. Christianne Elisabete da Costa Rodrigues.
- 5) *Controle de Processos* (Processes Control). Undergraduate subject of Food Engineering course (1<sup>st</sup> semester, 2015), FZEA/USP, Pirassununga/SP, Brazil. Responsible: Professor Dr. Christianne Elisabete da Costa Rodrigues.

## **6.5. Participation in committees**

- 1) Student representative of the Postgraduate Committee (CPG), FZEA/USP (2015).
- 2) Substitute student representative of the Coordinating Committee of the Food Engineering Program (CCPEA), FZEA/USP (2015).
- 3) Treasurer of the Postgraduate Association (APG), FZEA/USP, (management 2011/2012).
- 4) Treasurer of the Postgraduate Association (APG), FZEA/USP, (management 2013/2014).
- 5) Treasurer of the Postgraduate Association (APG), FZEA/USP, (management 2014/2015).
- 6) Treasurer of the Postgraduate Association (APG), FZEA/USP, (management 2015/2016).

## **6.6. Participation as examiner**

- 1) 21° *Simpósio Internacional de Iniciação Científica da Universidade de São Paulo* (SIICUSP), Agrarian Sciences area, Piracicaba/SP, Brazil, 2013.
- 2) 22° *Simpósio Internacional de Iniciação Científica da Universidade de São Paulo* (SIICUSP), Food Engineering area (1<sup>st</sup> stage), Pirassununga/SP, Brazil, 2014.

## **6.7. Involvement in events organization**

- 1) Lecture: *Aspectos e exigências atuais de sustentabilidade nas grandes indústrias de bebidas*, FZEA/USP, Pirassununga/SP, Brasil, 2011.
- 2) Workshop APG/FZEA – *Pós-Graduação e Ensino*, FZEA/USP, Pirassununga/SP, Brasil, 2013.
- 3) *V Colóquios da APG: Como elaborar um memorial circunstanciado e curriculum*, FZEA/USP, Pirassununga/SP, Brasil, 2015.

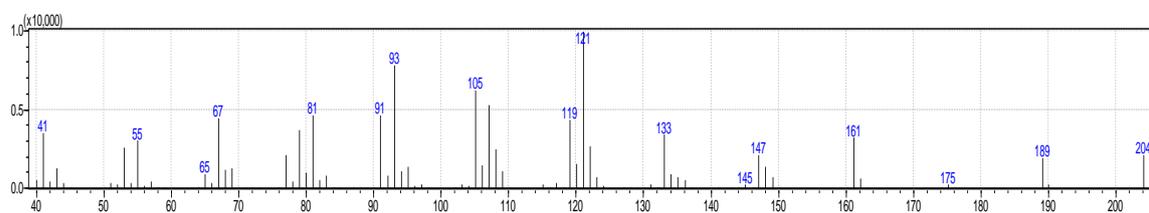
## **6.8. Participation as examiner jury**

- 1) Jury of the project of the undergraduate subject *Planejamento e Projetos II* (Planning and Projects II), Food Engineering course, FZEA/USP, Pirassununga/SP, Brazil. Project team: Mr. Drink, 2011.
- 2) Jury of the project of the undergraduate subject *Planejamento e Projetos II* (Planning and Projects II), Food Engineering course, FZEA/USP, Pirassununga/SP, Brazil. Project team: Top Bread, 2011.
- 3) Jury of the Supervised Internship I report and defense, Quality Control area, undergraduate student: Diego de Oliveira Fiorio, FZEA/USP, Pirassununga/SP, Brazil, 2012.
- 4) Jury of the Supervised Internship I report and defense, Production and Quality Control area, undergraduate student: Guilherme Rodrigues da Silva Alcantara, FZEA/USP, Pirassununga/SP, Brazil, 2012.

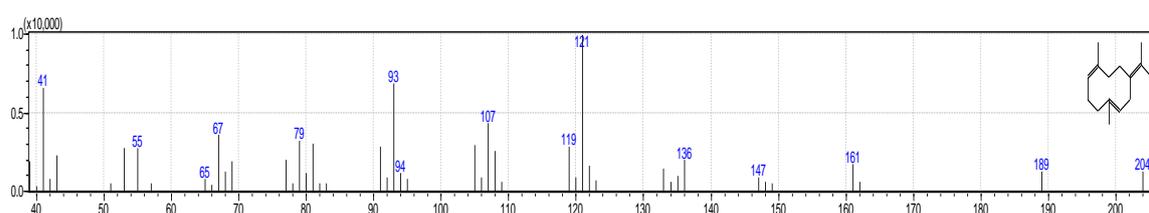
- 5) Jury of the Supervised Internship I report and defense, Technical Sales area, undergraduate student: Lucas Debortolli Cardozo Curto, FZEA/USP, Pirassununga/SP, Brazil, 2012.
- 6) Jury of the Supervised Internship I report and defense, Quality Control area, undergraduate student: Gabrielle Stival Asséf, FZEA/USP, Pirassununga/SP, Brazil, 2013.
- 7) Jury of the Supervised Internship I report and defense, Quality Control area, undergraduate student: Samuel Park, FZEA/USP, Pirassununga/SP, Brazil, 2013.
- 8) Jury of the Supervised Internship I report and defense, Supply Chain – Cold Chain area, undergraduate student: Larissa Lopes Venâncio, FZEA/USP, Pirassununga/SP, Brazil, 2014.
- 9) Jury of the Supervised Internship I report and defense, Research and Development area, undergraduate student: Martin Emil Erismann Teschke, FZEA/USP, Pirassununga/SP, Brazil, 2014.
- 10) Jury of the Supervised Internship I report and defense, Job Rotation area, undergraduate student: Leonardo Kenzo Narumiya, FZEA/USP, Pirassununga/SP, Brazil, 2015.
- 11) Jury of the Supervised Internship I report and defense, creation and application of aromas area, undergraduate student: Vanessa Akkari Guedes, FZEA/USP, Pirassununga/SP, Brazil, 2017.

## APPENDIX I: Mass spectra from the GC-MS analysis

The mass spectra for the pure component and the analyte, compared for the identification of some the components in the crude citrus essential oils by GC-MS analysis (Tables 2 from Chapters I and IV), are presented in the figures as follows:

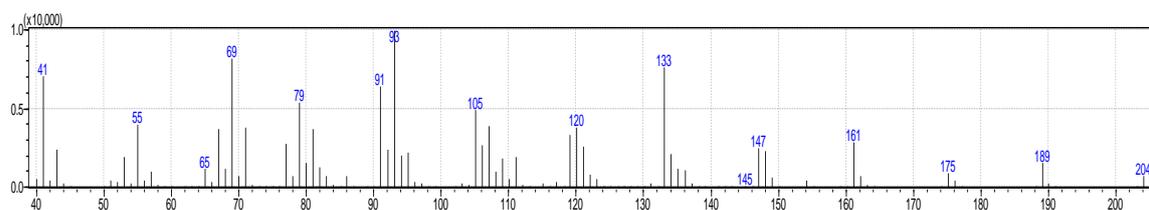


(a)

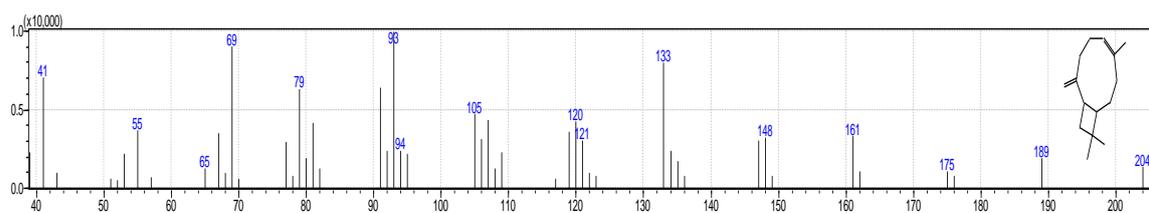


(b)

Figure A1: Mass spectra of: (a) analyte; (b) germacrene from NIST library. 92% of similarity.

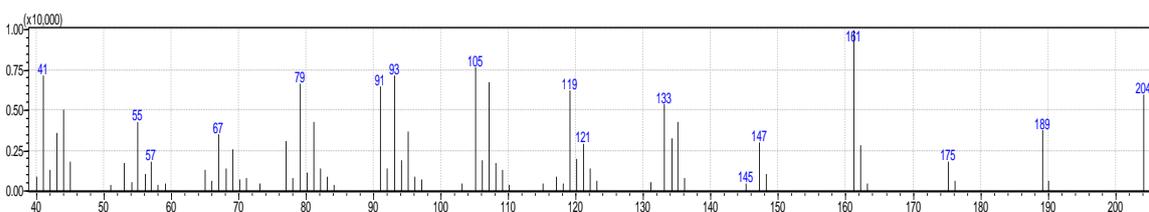


(a)

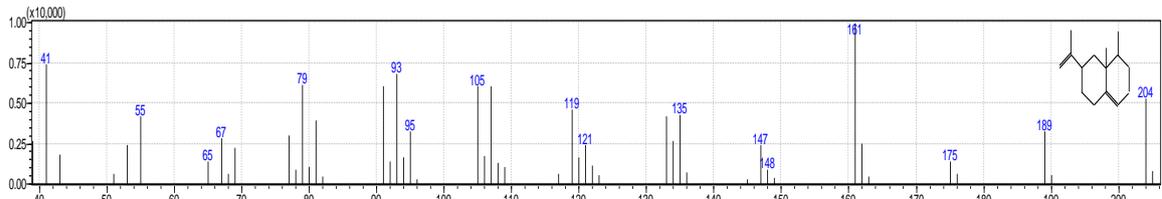


(b)

Figure A2: Mass spectra of: (a) analyte; (b)  $\beta$ -cariophyllene from NIST library. 93% of similarity.

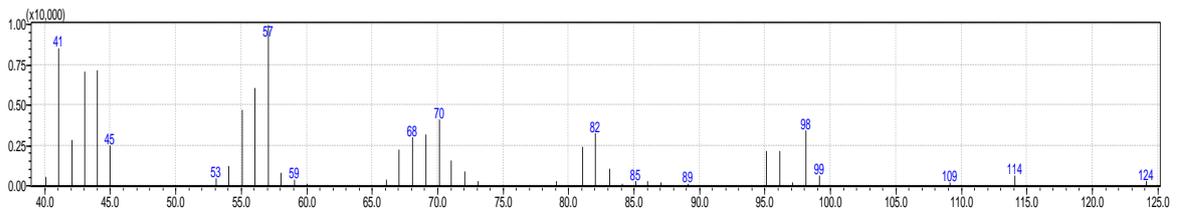


(a)

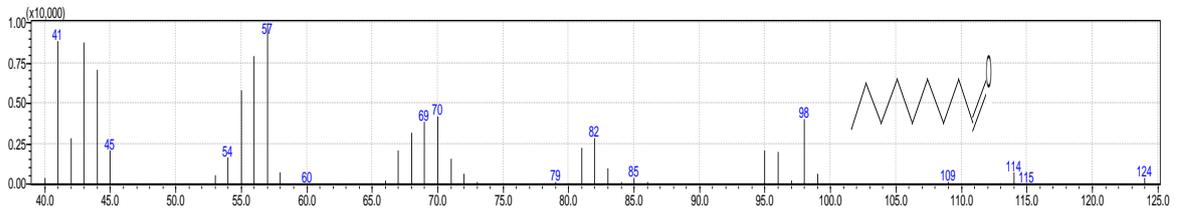


(b)

Figure A3: Mass spectra of: (a) analyte; (b) valencene from NIST library. 90% of similarity.

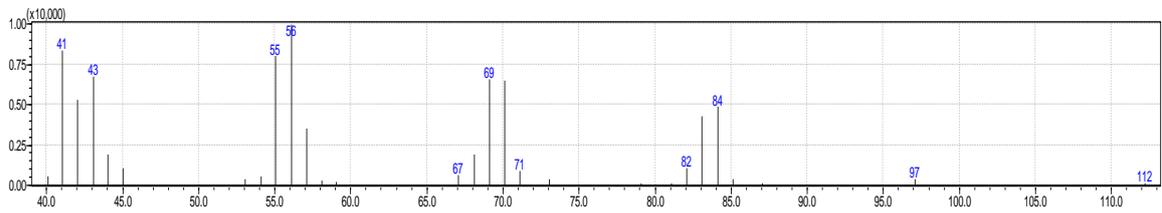


(a)

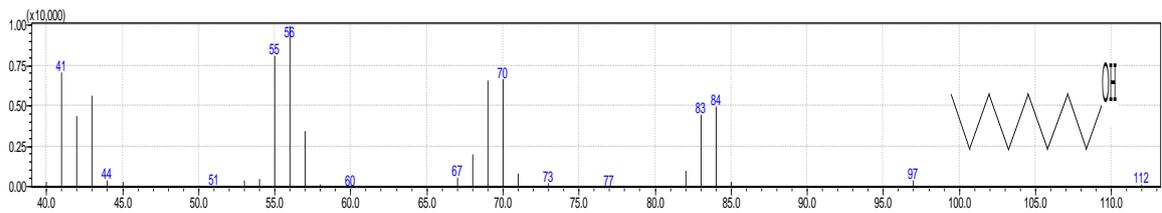


(b)

Figure A4: Mass spectra of: (a) analyte; (b) nonanal from NIST library. 97% of similarity.

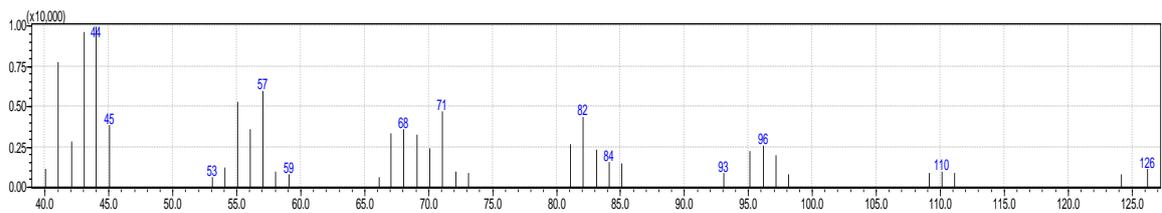


(a)

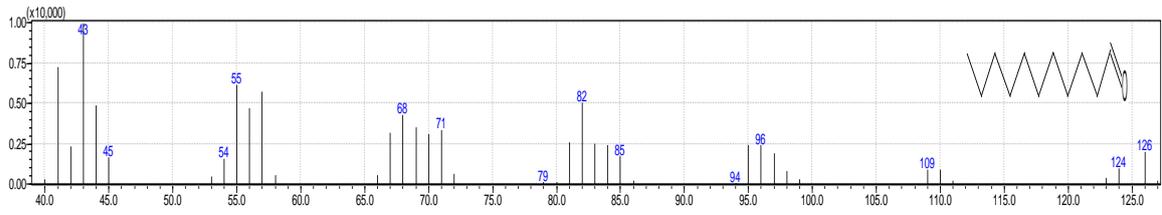


(b)

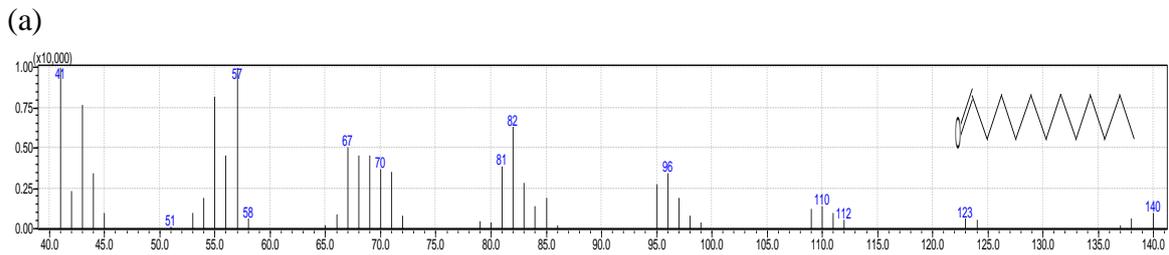
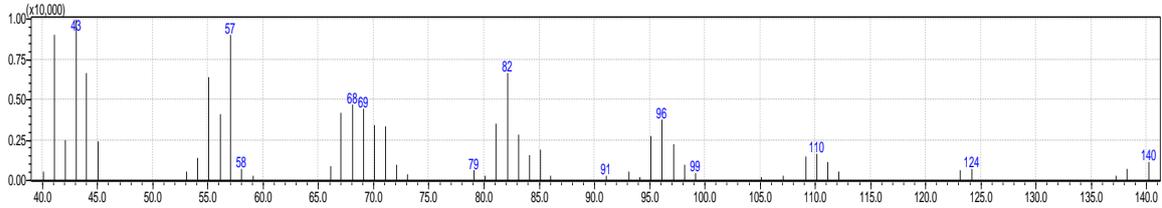
Figure A5: Mass spectra of: (a) analyte; (b) octanol from NIST library. 97% of similarity.



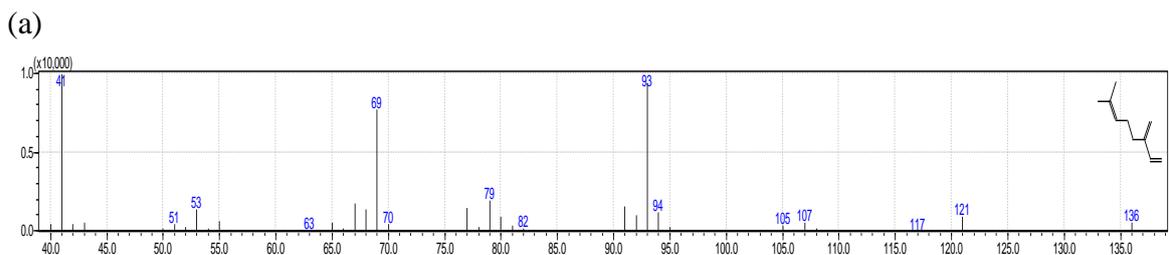
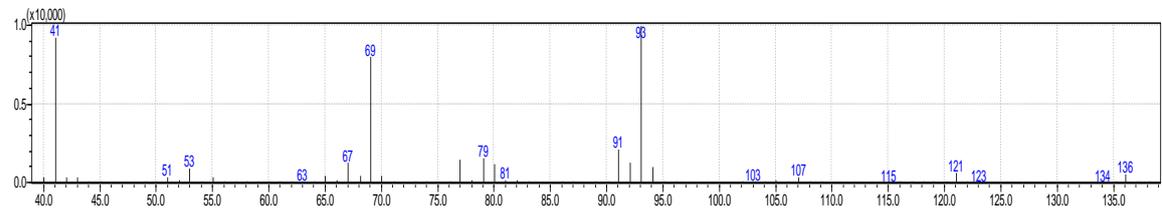
(a)



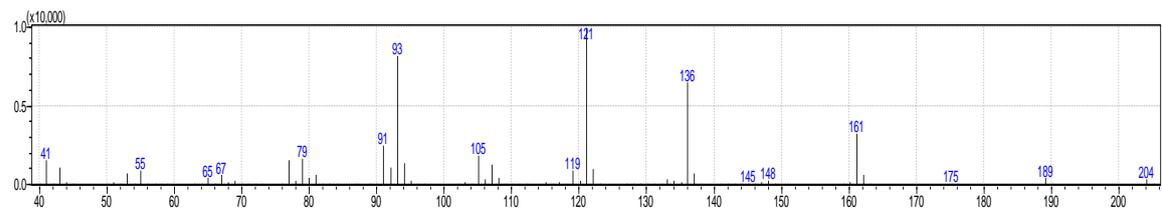
(b)  
Figure A6: Mass spectra of: (a) analyte; (b) undecanal from NIST library. 89% of similarity.



(b)  
Figure A7: Mass spectra of: (a) analyte; (b) dodecanal from NIST library. 95% of similarity.



(b)  
Figure A8: Mass spectra of: (a) analyte; (b) myrcene from NIST library. 96% of similarity.



(a)

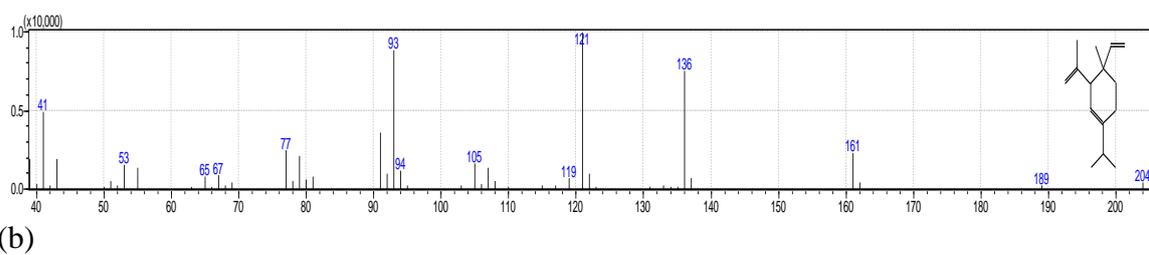
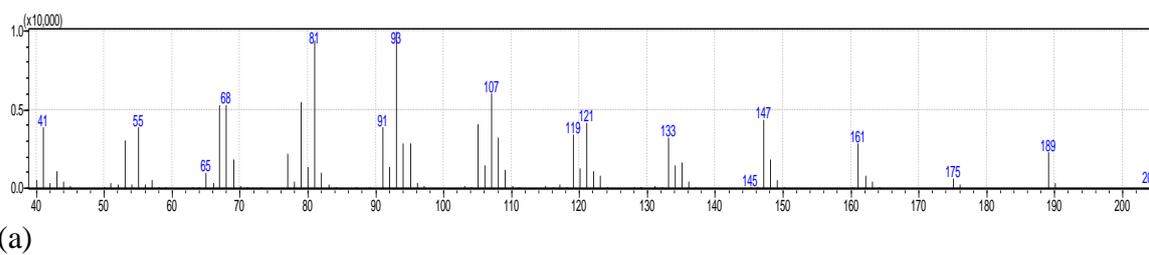


Figure A9: Mass spectra of: (a) analyte; (b)  $\delta$ -elemene from NIST library. 92% of similarity.



(a)

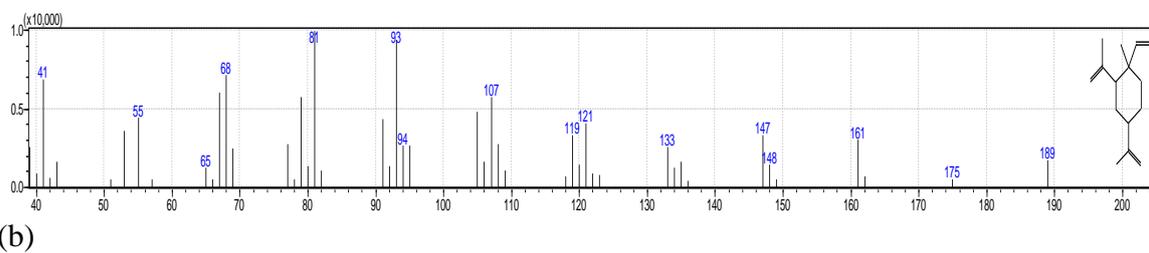
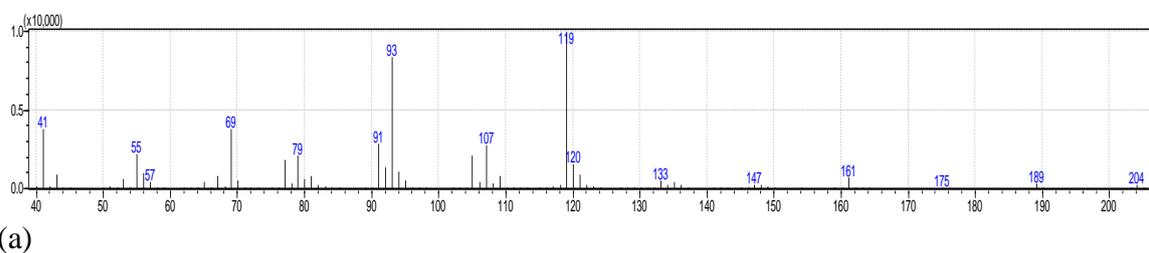


Figure A10: Mass spectra of: (a) analyte; (b)  $\beta$ -elemene from NIST library. 95% of similarity.



(a)

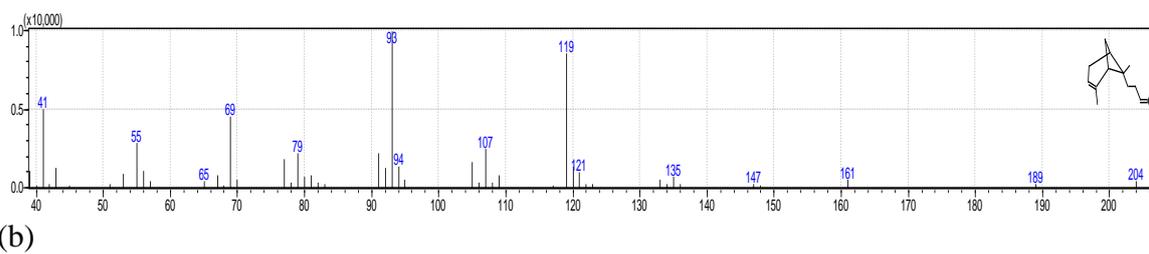
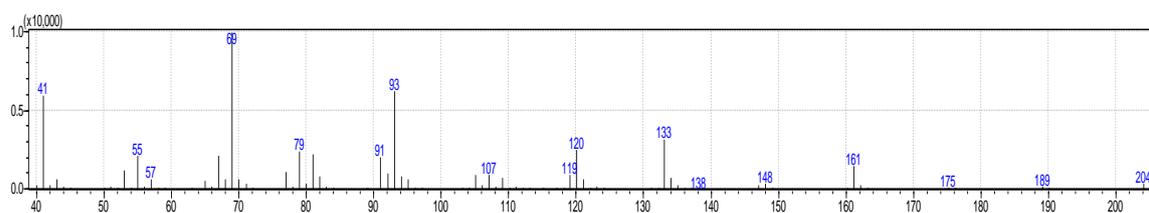
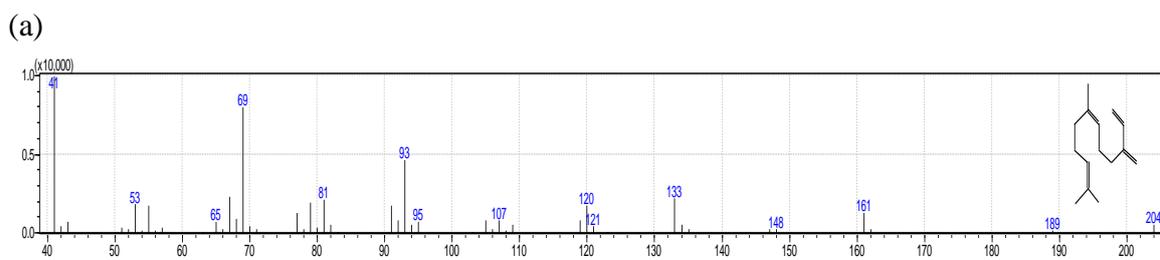
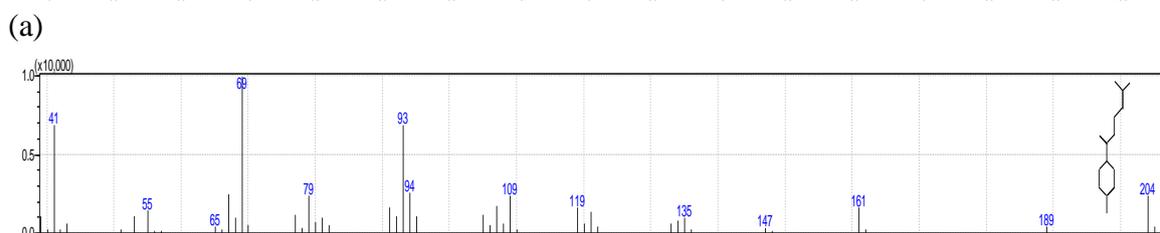
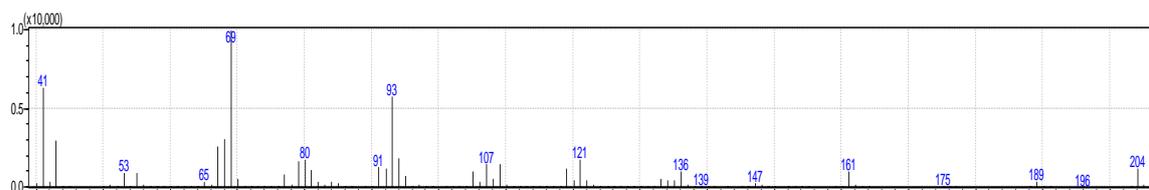


Figure A11: Mass spectra of: (a) analyte; (b)  $\alpha$ -bergamotene from NIST library. 95% of similarity.

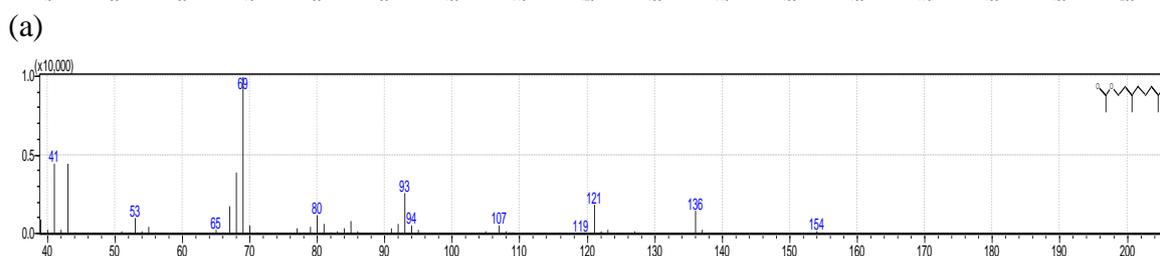
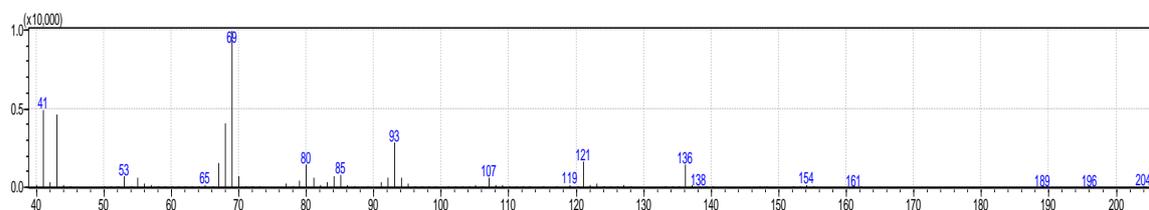




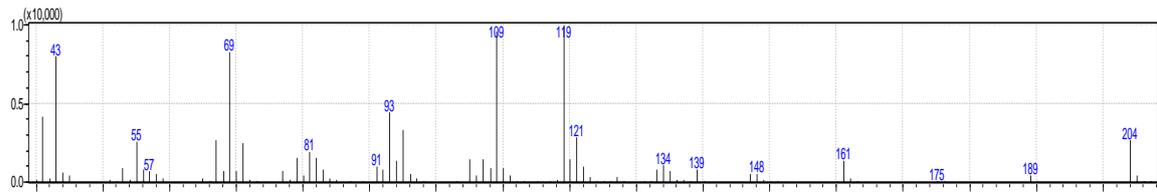
(b)  
Figure A12: Mass spectra of: (a) analyte; (b)  $\beta$ -farnesene from NIST library. 93% of similarity.



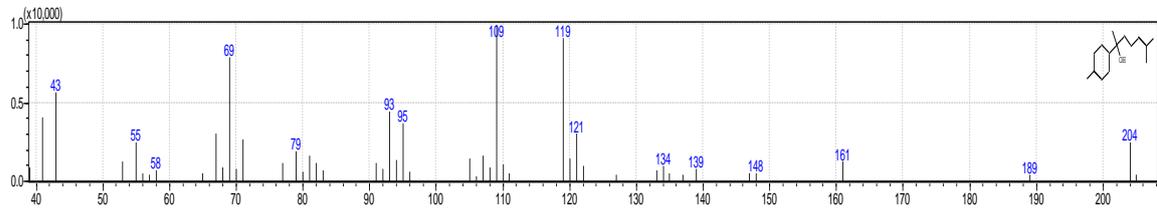
(b)  
Figure A13: Mass spectra of: (a) analyte; (b)  $\beta$ -bisabolene from NIST library. 92% of similarity.



(b)  
Figure A14: Mass spectra of: (a) analyte; (b) geranyl acetate from NIST library. 97% of similarity.



(a)



(b)

Figure A15: Mass spectra of: (a) analyte; (b) bisabolol from NIST library. 96% of similarity.

## APPENDIX II: Calibration curves for liquid samples

The quantification of the volatile components in the liquid crude citrus essential oils and the phases from the liquid–liquid equilibrium, in mass fraction, was done by external standardization (calibration curves). Table A1 shows the mass fractions of each component injected in gas chromatograph using a DB-FFAP capillary column and their respective area peak. The calibration curves were acquired by the linear adjustment between the mass fractions ( $w$ ) and the peak areas.

**Table A1:** Mass fractions injected in the capillary column and their respective peak area.

Orange systems					
Ethanol		Limonene		Linalool	
$w$	<i>Peak Area</i>	$w$	<i>Peak Area</i>	$w$	<i>Peak Area</i>
0.0003	28973.6	0.0003	52568.3	0.0003	50706.6
0.0005	50724.1	0.0005	108146.5	0.0006	94602.9
0.0052	567415.5	0.0050	1222523.3	0.0052	1440086.9
0.0097	1030332.9	0.0101	2404237.0	0.0098	1965579.8
0.0197	2154197.8	0.0202	4927349.1	0.0203	4217563.5
0.0491	5319940.5	0.0502	12305974.3	0.0502	10932946.1
0.1001	11197411.6	0.0974	25010969.8	0.0988	22290095.2
0.1955	22365533.2	0.1981	52672315.9	0.1993	46738783.2
0.3155	33871618.1	0.3191	83293398.5		
Lemon/lime systems					
Ethanol		$\beta$ -Pinene		Limonene	
$w$	<i>Peak Area</i>	$w$	<i>Peak Area</i>	$w$	<i>Peak Area</i>
0.0003	18041.6	0.0003	14609.55	0.0002	12481.1
0.0005	13533.55	0.0005	14489.1	0.0006	16474.8
0.0047	139216.4	0.0049	294188.5	0.0061	334562.85
0.0086	332515.05	0.0101	817369.3	0.0084	659507.8
0.0183	619758.85	0.0209	1509667.5	0.0200	1481453.95
0.0500	1821767.2	0.0514	3872485.5	0.0468	3473434.45
0.1029	4787446.1	0.0998	9783238.3	0.1019	9545320.03
0.2021	8747164.5	0.1999	21389640	0.1958	20581227.7
0.3333	13683677	0.3333	34174659	0.3316	33281800.8
$\gamma$ -Terpinene		Neral		Geranial	
$w$	<i>Peak Area</i>	$w$	<i>Peak Area</i>	$w$	<i>Peak Area</i>
0.0003	15510.45	0.0001	4176.4	0.0002	7181.8
0.0005	14622.4	0.0002	2935.2	0.0003	4998.6
0.0050	292698	0.0026	106751.5	0.0046	189833.3
0.0093	745666.05	0.0038	198142.0	0.0067	351965.7
0.0193	1478306.2	0.0070	415666.1	0.0122	737836.7
0.0509	3844837.5	0.0194	1088363.0	0.0340	1911159.5
0.0972	9322989.4	0.0364	2650712.0	0.0638	4645831.3
0.1959	18656523	0.0717	5534295.0	0.1256	9696530.0
0.3259	29265391	0.1204	9210406.7	0.2111	16049720.9

Since components with similar chemical structure tend to exhibit the same behavior in liquid mixtures, for the real systems the limonene calibration curve was used to quantify the other terpenes, when the other aldehydes were quantified using the geranial calibration curve and the alcohols (except ethanol) were quantified using the linalool calibration curve. The calibration curves are presented in Eqs. (A1) to (A9).

For orange systems:

$$w_{ethanol} = 9.1285 \times 10^{-9} \times Area \quad R^2 = 0.9988 \quad (A1)$$

$$w_{limonene} = 3.8204 \times 10^{-9} \times Area \quad R^2 = 0.9997 \quad (A2)$$

$$w_{linalool} = 4.3123 \times 10^{-9} \times Area \quad R^2 = 0.9992 \quad (A3)$$

For lemon/lime systems:

$$w_{ethanol} = 2.3846 \times 10^{-8} \times Area \quad R^2 = 0.9975 \quad (A4)$$

$$w_{\beta\text{-pinene}} = 9.7087 \times 10^{-9} \times Area \quad R^2 = 0.9967 \quad (A5)$$

$$w_{limonene} = 9.9189 \times 10^{-9} \times Area \quad R^2 = 0.9970 \quad (A6)$$

$$w_{\gamma\text{-terpinene}} = 1.3135 \times 10^{-8} \times Area \quad R^2 = 0.9979 \quad (A7)$$

$$w_{neral} = 1.3135 \times 10^{-8} \times Area \quad R^2 = 0.9975 \quad (A8)$$

$$w_{geranial} = 1.3191 \times 10^{-8} \times Area \quad R^2 = 0.9976 \quad (A9)$$

### APPENDIX III: Calibration curves for gas samples

Ethanol, limonene,  $\alpha$ -pinene,  $\beta$ -pinene,  $\gamma$ -terpinene, octanal, nonanal, decanal, citral, citronellal,  $\alpha$ -terpineol, linalool, nerol and geraniol, were used for the construction of calibration curves, which were used for the quantification of the components in the gas phase, by external standard method. For the achievement of the calibration curve for each component, headspace analysis of the pure component was done in different split ratios, under the same gas chromatography conditions described in Chapters II and IV.

The calibration curves relate the mass of a component  $i$  inside the GC column ( $m_i$ ) to its peak area obtained from the chromatograms. The concentration of the component  $i$  was calculated by Eq. (A10).

$$C_i = \frac{m_i}{V_{column}} \quad (\text{A10})$$

where  $m_i$  is the mass of the component  $i$  inside the GC column (g) and  $V_{column}$  is the volume of the sample inserted in the GC column (m<sup>3</sup>).

For the determination of  $m_i$  values, the general ideal gas law, Eq. (A11), was used.

$$P_i^{sat} \cdot V_{column} = n_i \cdot R \cdot T \quad (\text{A11})$$

where  $P_i^{sat}$  is the vapor pressure of the component  $i$  (Pa),  $n_i$  is the number of moles of the component  $i$  injected into the column,  $R$  is the gas universal constant (J/mol·K) and  $T$  is the absolute temperature (K). The  $n_i$  was calculated by Eq. (A12).

$$n_i = \frac{m_i}{M_i} \quad (\text{A12})$$

where  $M_i$  is the molar mass of the component  $i$  (g/mol). Using the Eq. (A12) in Eq. (A11):

$$P_i^{sat} \cdot V_{column} = \frac{m_i}{M_i} \cdot R \cdot T \quad (\text{A13})$$

$$m_i = \frac{P_i^{sat} \cdot V_{column} \cdot M_i}{R \cdot T} \quad (\text{A14})$$

$$V_{injected} = V_{column} + V_{vent} \quad (\text{A15})$$

where  $V_{vent}$  is the volume that was not injected in the GC column, according to the split ratio. Then:

$$split = \frac{V_{vent}}{V_{column}} \quad (\text{A16})$$

$$V_{column} = \frac{V_{injected}}{split} \quad (A17)$$

$$V_{injected} = V_{column} \cdot split + V_{column} \quad (A18)$$

$$V_{injected} = V_{column} \cdot (1 + split) \quad (A19)$$

$$V_{column} = \frac{V_{injected}}{(1 + split)} \quad (A20)$$

Combining Eq. (A19) and Eq. (20):

$$m_i = \frac{P_i^{sat} \cdot V_{injected} \cdot M_i}{R \cdot T \cdot (split + 1)} \quad (A21)$$

Then, from Eq. (A21), the concentration of a component  $i$  (g/m<sup>3</sup>) in the headspace was calculated by Eq. (A22):

$$C_i = \frac{m_i}{V_{injected}} \cdot (1 + split) \quad (A22)$$

All the splits ratios, calculated  $m_i$  (in g) and the experimental peak areas of each component used for the construction of the calibration curves are exposed in Table A1.

**Table A2:** *Splits* ratios, masses of the components inside the GC column ( $m_i$ ) and the corresponding experimental peak area used for the calibration curves.

Terpenes			Alcohols						Aldehydes					
Limonene			Ethanol			Geraniol			Citronellal			Decanal		
<i>Split</i>	$m_i$ (g)	<i>Peak Area</i>	<i>Split</i>	$m_i$ (g)	<i>Peak Area</i>	<i>Split</i>	$m_i$ (g)	<i>Peak Area</i>	<i>Split</i>	$m_i$ (g)	<i>Peak Area</i>	<i>Split</i>	$m_i$ (g)	<i>Peak Area</i>
300	$7.54 \times 10^{-9}$	60418	400	$7.32 \times 10^{-8}$	236743	500	$9.94 \times 10^{-11}$	1142	400	$1.16 \times 10^{-9}$	9103	500	$3.46 \times 10^{-10}$	5959
250	$9.04 \times 10^{-9}$	77117	350	$8.37 \times 10^{-8}$	267922	400	$1.24 \times 10^{-10}$	1329	300	$1.54 \times 10^{-9}$	11279	400	$4.32 \times 10^{-10}$	8325
200	$1.13 \times 10^{-8}$	106287	300	$9.76 \times 10^{-8}$	319739	300	$1.65 \times 10^{-10}$	1714	250	$1.85 \times 10^{-9}$	13642	300	$5.75 \times 10^{-10}$	11914
200	$1.13 \times 10^{-8}$	117306	250	$1.17 \times 10^{-7}$	371923	200	$2.48 \times 10^{-10}$	2366	200	$2.31 \times 10^{-9}$	16561	200	$8.61 \times 10^{-10}$	18915
150	$1.50 \times 10^{-8}$	147606	200	$1.46 \times 10^{-7}$	472557	100	$4.93 \times 10^{-10}$	4690	100	$4.60 \times 10^{-9}$	31341	100	$1.71 \times 10^{-9}$	38010
100	$2.25 \times 10^{-8}$	237741	150	$1.94 \times 10^{-7}$	651321	45	$1.08 \times 10^{-9}$	10833	75	$6.11 \times 10^{-9}$	41814	55	$3.09 \times 10^{-9}$	64385
50	$4.45 \times 10^{-8}$	461730												
$\alpha$ -Pinene			Linalool			Nerol			Neral			Octanal		
<i>Split</i>	$m_i$ (g)	<i>Peak Area</i>	<i>Split</i>	$m_i$ (g)	<i>Peak Area</i>	<i>Split</i>	$m_i$ (g)	<i>Peak Area</i>	<i>Split</i>	$m_i$ (g)	<i>Peak Area</i>	<i>Split</i>	$m_i$ (g)	<i>Peak Area</i>
400	$1.74 \times 10^{-8}$	56583	800	$3.31 \times 10^{-10}$	7797	500	$4.40 \times 10^{-11}$	1142	500	$2.98 \times 10^{-10}$	1438	800	$2.03 \times 10^{-9}$	12522
300	$2.31 \times 10^{-8}$	72359	700	$3.79 \times 10^{-10}$	7901	400	$5.50 \times 10^{-11}$	1329	400	$3.73 \times 10^{-10}$	1753	700	$2.32 \times 10^{-9}$	12809
250	$2.77 \times 10^{-8}$	87205	600	$4.42 \times 10^{-10}$	8942	300	$7.33 \times 10^{-11}$	1714	300	$4.97 \times 10^{-10}$	2305	600	$2.71 \times 10^{-9}$	12865
200	$3.46 \times 10^{-8}$	108323	500	$5.30 \times 10^{-10}$	10841	200	$1.10 \times 10^{-10}$	2366	200	$7.44 \times 10^{-10}$	3380	500	$3.25 \times 10^{-9}$	16657
150	$4.61 \times 10^{-8}$	135539	400	$6.62 \times 10^{-10}$	13121	100	$2.18 \times 10^{-10}$	4690	100	$1.48 \times 10^{-9}$	6706	400	$4.06 \times 10^{-9}$	20262
100	$6.89 \times 10^{-8}$	208961	300	$8.82 \times 10^{-10}$	17415	45	$4.80 \times 10^{-10}$	10833	55	$2.67 \times 10^{-9}$	12505	300	$5.41 \times 10^{-9}$	27945
			100	$2.63 \times 10^{-9}$	51535							250	$6.48 \times 10^{-9}$	43249
												100	$1.61 \times 10^{-8}$	105836
$\beta$ -Pinene			Octanol			$\alpha$ -Terpineol			Geranial			Nonanal		
<i>Split</i>	$m_i$ (g)	<i>Peak Area</i>	<i>Split</i>	$m_i$ (g)	<i>Peak Area</i>	<i>Split</i>	$m_i$ (g)	<i>Peak Area</i>	<i>Split</i>	$m_i$ (g)	<i>Peak Area</i>	<i>Split</i>	$m_i$ (g)	<i>Peak Area</i>
300	$1.43 \times 10^{-8}$	85612	500	$2.22 \times 10^{-10}$	3362	500	$1.40 \times 10^{-10}$	3223	500	$2.98 \times 10^{-10}$	1450	500	$1.13 \times 10^{-9}$	5959
250	$1.71 \times 10^{-8}$	101139	400	$2.77 \times 10^{-10}$	4204	400	$1.75 \times 10^{-10}$	4854	400	$3.73 \times 10^{-10}$	1784	400	$1.41 \times 10^{-9}$	8325
200	$2.14 \times 10^{-8}$	124888	300	$3.70 \times 10^{-10}$	5725	300	$2.33 \times 10^{-10}$	5995	300	$4.97 \times 10^{-10}$	2380	300	$1.88 \times 10^{-9}$	11914
150	$2.84 \times 10^{-8}$	158617	200	$5.53 \times 10^{-10}$	8748	200	$3.49 \times 10^{-10}$	9342	200	$7.44 \times 10^{-10}$	3455	200	$2.82 \times 10^{-9}$	18915
100	$4.25 \times 10^{-8}$	242881	100	$1.10 \times 10^{-9}$	16380	100	$6.95 \times 10^{-10}$	17004	100	$1.48 \times 10^{-9}$	7005	100	$5.60 \times 10^{-9}$	38010
80	$5.30 \times 10^{-8}$	302378	45	$2.42 \times 10^{-9}$	36171	40	$1.71 \times 10^{-9}$	39622	55	$2.67 \times 10^{-9}$	13067	55	$1.01 \times 10^{-8}$	64385
$\gamma$ -Terpinene														
<i>Split</i>	$m_i$ (g)	<i>Peak Area</i>												
300	$5.29 \times 10^{-9}$	31293												
250	$6.35 \times 10^{-9}$	43646												
200	$7.93 \times 10^{-9}$	60449												
150	$1.05 \times 10^{-8}$	86211												
100	$1.58 \times 10^{-8}$	138184												
40	$3.89 \times 10^{-8}$	320542												

The calibration curves used to quantify the components identified in the gas samples are shown in Eqs. (A23) to (A38).

Terpenes:

$$m_{\text{limonene}} = 9.7406 \times 10^{-14} \times \text{Area} \quad R^2 = 0.9944 \quad (\text{A23})$$

$$m_{\alpha\text{-pinene}} = 3.2819 \times 10^{-13} \times \text{Area} \quad R^2 = 0.9979 \quad (\text{A24})$$

$$m_{\beta\text{-pinene}} = 1.7478 \times 10^{-13} \times \text{Area} \quad R^2 = 0.9992 \quad (\text{A25})$$

$$m_{\gamma\text{-terpinene}} = 1.2123 \times 10^{-13} \times \text{Area} \quad R^2 = 0.9952 \quad (\text{A26})$$

Alcohols:

$$m_{\text{ethanol}} = 3.0530 \times 10^{-13} \times \text{Area} \quad R^2 = 0.9983 \quad (\text{A27})$$

$$m_{\text{linalool}} = 5.0628 \times 10^{-14} \times \text{Area} \quad R^2 = 0.9988 \quad (\text{A28})$$

$$m_{\text{octanol}} = 6.6688 \times 10^{-14} \times \text{Area} \quad R^2 = 0.9997 \quad (\text{A29})$$

$$m_{\text{geraniol}} = 1.0060 \times 10^{-13} \times \text{Area} \quad R^2 = 0.9988 \quad (\text{A30})$$

$$m_{\text{geraniol}} = 4.4584 \times 10^{-14} \times \text{Area} \quad R^2 = 0.9988 \quad (\text{A31})$$

$$m_{\alpha\text{-terpineol}} = 3.8800 \times 10^{-14} \times \text{Area} \quad R^2 = 0.9988 \quad (\text{A32})$$

Aldehydes:

$$m_{\text{citronella}} = 1.4443 \times 10^{-13} \times \text{Area} \quad R^2 = 0.9977 \quad (\text{A33})$$

$$m_{\text{neral}} = 2.1526 \times 10^{-13} \times \text{Area} \quad R^2 = 0.9977 \quad (\text{A34})$$

$$m_{\text{geranial}} = 2.0643 \times 10^{-13} \times \text{Area} \quad R^2 = 0.9994 \quad (\text{A35})$$

$$m_{\text{octanal}} = 1.5725 \times 10^{-13} \times \text{Area} \quad R^2 = 0.9977 \quad (\text{A36})$$

$$m_{\text{nonanal}} = 1.5466 \times 10^{-13} \times \text{Area} \quad R^2 = 0.9822 \quad (\text{A37})$$

$$m_{\text{decanal}} = 4.7300 \times 10^{-14} \times \text{Area} \quad R^2 = 0.9977 \quad (\text{A38})$$

## APPENDIX IV: Odor Detection Thresholds

For the determination of the ODTs, a panel with different people belonging to the LSRE were recruited and the threshold dilution factors of each panelist were achieved by sensorial analysis through an olfactometer equipment (detailed procedure and the conditions used for the analyses are described in the Chapters II and IV). The answers of the panelists for each component are presented in Tables A2 to A5.

### (a) Citral

**Table A3:** Threshold dilution factors ( $Z_{k,i}^{thr}$ ) for all panelists for citral.

Sequence	P1	P2	P3	P4
1	226.27	226.27	452.55	452.55
2	452.55	452.55	226.27	452.55
3	226.27	452.55	113.14	-

$$M_{citral} = \frac{\sum_{k=1}^4 \sum_{l=1}^3 \log_{10}(Z_{k,l}^{thr})}{L} = 2.49$$

$$Z_{citral}^{thr} = 10^M = 310.08$$

$$C_{citral}^0 = 5.98 \text{ mg/m}^3$$

$$ODT_{citral} = \frac{C_{citral}^0}{Z_{citral}^{thr}} 1.93 \times 10^{-5} \text{ g/m}^3$$

### (b) Citronellal

**Table A4:** Threshold dilution factors ( $Z_{k,i}^{thr}$ ) for all panelists for citronellal.

Sequence	P1	P2	P3	P4
1	452.55	452.55	452.55	452.55
2	226.27	452.55	452.55	226.27
3	226.27	452.55	452.55	452.55
4	452.55	452.55	226.27	452.55
5	452.55	452.55	452.55	-

$$M_{\text{citronellid}} = \frac{\sum_{k=1}^4 \sum_{l=1}^3 \log_{10}(Z_{k,l}^{thr})}{L} = 2.59$$

$$Z_{\text{citronellid}}^{thr} = 10^M = 391.10$$

$$C_{\text{citronellid}}^0 = 9.29 \text{ mg/m}^3$$

$$ODT_{\text{citronellid}} = \frac{C_{\text{citronellid}}^0}{Z_{\text{citronellid}}^{thr}} 2.38 \times 10^{-5} \text{ g/m}^3$$

### (c) $\beta$ -Pinene

**Table A5:** Threshold dilution factors ( $Z_{k,i}^{thr}$ ) for all panelists for  $\beta$ -pinene.

Sequence	P1	P2	P3	P4
1	28.28	28.28	28.28	28.28
2	28.28	113.14	28.28	28.28
3	28.28	28.28	14.14	28.28

$$M_{\beta\text{-pinene}} = \frac{\sum_{k=1}^4 \sum_{l=1}^3 \log_{10}(Z_{k,l}^{thr})}{L} = 1.48$$

$$Z_{\beta\text{-pinene}}^{thr} = 10^M = 29.97$$

$$C_{\beta\text{-pinene}}^0 = 257.62 \text{ mg/m}^3$$

$$ODT_{\beta\text{-pinene}} = \frac{C_{\beta\text{-pinene}}^0}{Z_{\beta\text{-pinene}}^{thr}} 8.60 \times 10^{-3} \text{ g/m}^3$$

### (d) $\gamma$ -Terpinene

**Table A6:** Threshold dilution factors ( $Z_{k,i}^{thr}$ ) for all panelists for  $\gamma$ -terpinene

Sequence	P1	P2	P3	P4
1	28.28	113.14	56.57	28.28
2	56.57	113.14	56.57	56.57
3	56.57	113.14	113.14	28.28

$$M_{\gamma\text{-terpinene}} = \frac{\sum_{k=1}^4 \sum_{l=1}^3 \log_{10}(Z_{k,l}^{thr})}{L} = 1.78$$

$$Z_{\gamma\text{-terpinene}}^{thr} = 10^M = 59.93$$

$$C_{\gamma\text{-terpinene}}^0 = 95.58 \text{ mg/m}^3$$

$$ODT_{\gamma\text{-terpinene}} = \frac{C_{\gamma\text{-terpinene}}^0}{Z_{\gamma\text{-terpinene}}^{thr}} 1.59 \times 10^{-3} \text{ g/m}^3$$

**APPENDIX V: Molecules breaking for the UNIQUAC and GCVOL models.**

Group	Number of each group in the molecule																											
	Ethanol	$\alpha$ -Pinene	$\beta$ -Limonene	$\beta$ -Pinene	Myrcene	$\gamma$ -terpinene	$p$ -Cymene	Terpinolene	$\delta$ -Elemene	$\beta$ -Farnesene	$\beta$ -Bisabolene	Germacrene	Caryophyllene	Valencene	$\alpha$ -Bergamotene	Octanal	Nonanal	Citronellal	Linalool	Octanol	Decanal	Undecanal	Neral/Geraniol	Geranyl acetate	$\alpha$ -Terpineol	Dodecanal	Nerol/Geraniol	Bisabolol
UNIQUAC Model																												
CH <sub>3</sub>	1	3	2	2	2	3	3	3	4	4	3	4	3	3	4	1	1	3	3	1	1	1	3	4	3	1	3	4
CH <sub>2</sub>	1	2	3	3	2	2		3	2	3	5	5	5	5	4	6	7	3	2	7	8	9	2	2	3	10	3	5
CH		2	1	2		1	1		2		1		2	2	2			1							1			1
C=CH		1	1		1	2	2	2	1	3	2	3	1	1	2				1	1			2	2			2	2
C=CH <sub>2</sub>			1	1	2				2		1		1	1														
CH=O (aldehyde)																1	1	1			1	1	1				1	
C		1		1					1				1	1	1				1						1			1
OH	1																		1	1					1		1	1
CH=CH <sub>2</sub>										1									1									
CH = CH							1																					
CH <sub>2</sub> -O-C=O																									1			
GCVOL Model																												
-CH <sub>3</sub>	1	3	2	2	2	2	3	3	4	4	3	4	3	3	4	1	1	3	3	1	1	1	3	3	3	1	3	4
-CH <sub>2</sub> - (chain)					2					3	2				4	6	7	3	2	6	8	9	2	3		10	2	
>CH-							1		1						2			1										
C (chain)															1													
CH <sub>2</sub> =			1	1	2	1			2	1	1		1	1					1									2
-CH=		1	1		2	1	4	1	2	4	3	2	1	1	2				1	2			2	2	1		2	2
>C=		1	2	1	2	2	2	3	2	3	2	4	2	2	2			1	1				2	2	1		2	2
CH <sub>2</sub> (cyclic)		2	3	3		3		3	2		3	5	5	5											3			3
CH (cyclic)		2	1	2		1			1		1		2	2											1			1
C (cyclic)		1		1					1				1	1														
-CH <sub>2</sub> -OH	1																			1							1	
>CH-OH																												
-C-OH																			1						1			1
-CHO (aldehyde)																1	1	1			1	1	1			1		
CH <sub>3</sub> -COO (ester)																								1				

## APPENDIX VI: Composition profiles of the streams from the PRDC equipment

### (a) Assays using crude orange essential oil as feed

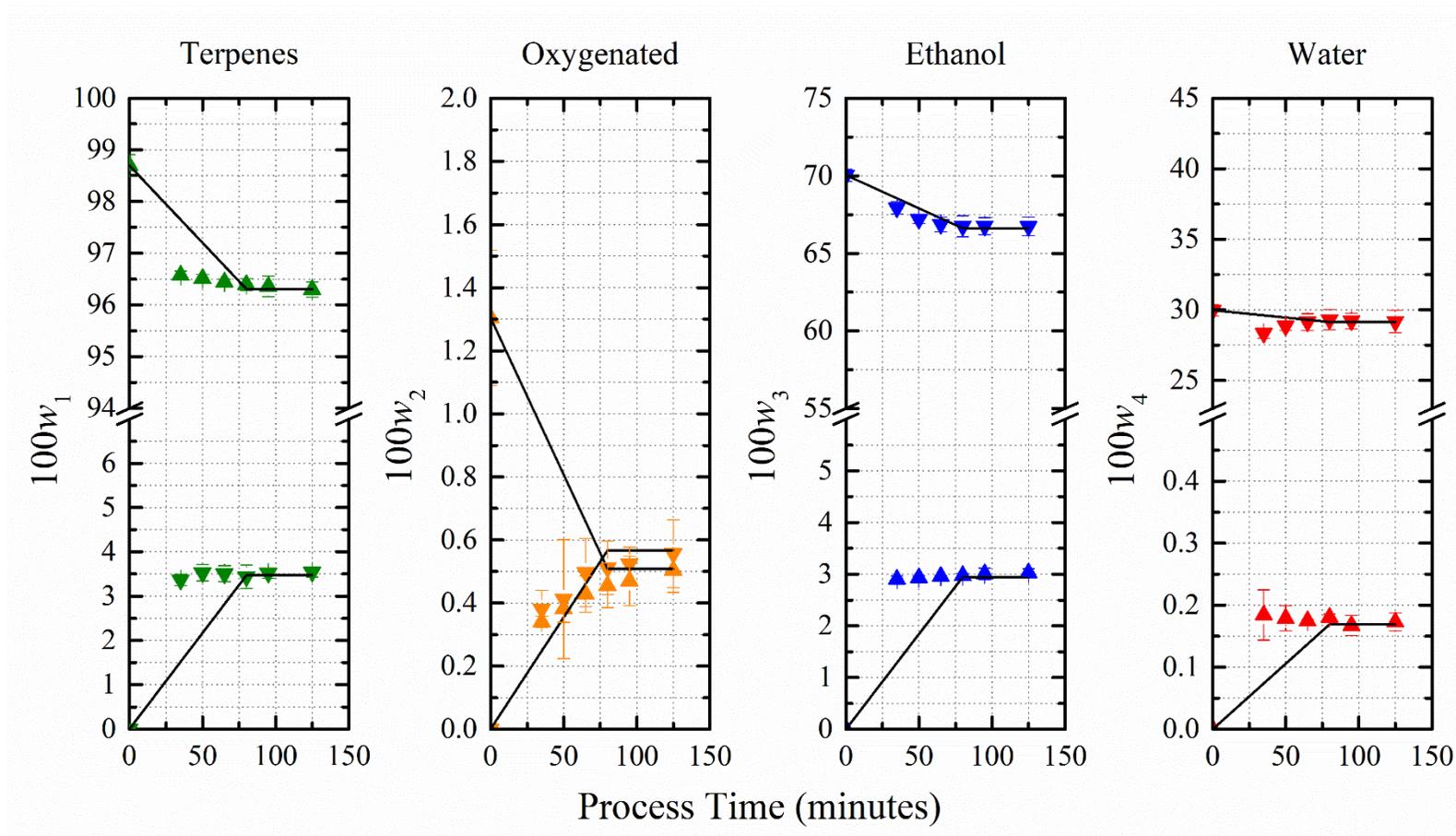


Figure A16: Composition profiles of the streams from the PRDC equipment, in mass percentage (100w), using ethanol + 30% (w/w) water as solvent. (1) terpenes; (2) oxygenated compounds; (3) ethanol; (4) water. (▲) raffinate stream; (▼), extract stream. The line (—) indicates the steady state.

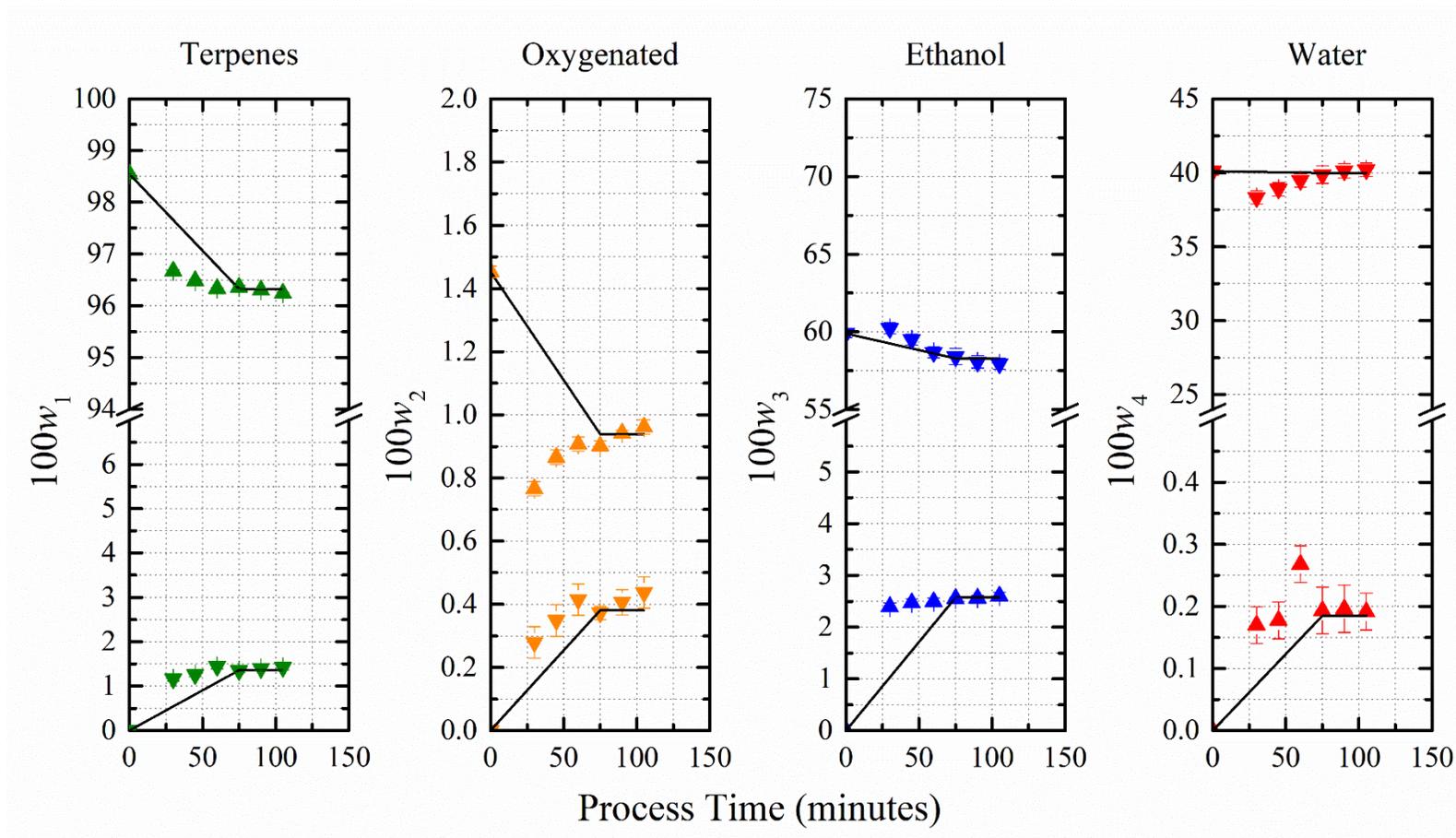


Figure A17: Composition profiles of the streams from the PRDC equipment, in mass percentage (100w), using ethanol + 40% (w/w) water as solvent. (1) terpenes; (2) oxygenated compounds; (3) ethanol; (4) water. (▲) raffinate stream; (▼), extract stream. The line (—) indicates the steady state.

**(b) Assays using crude acid lime essential oil as feed**

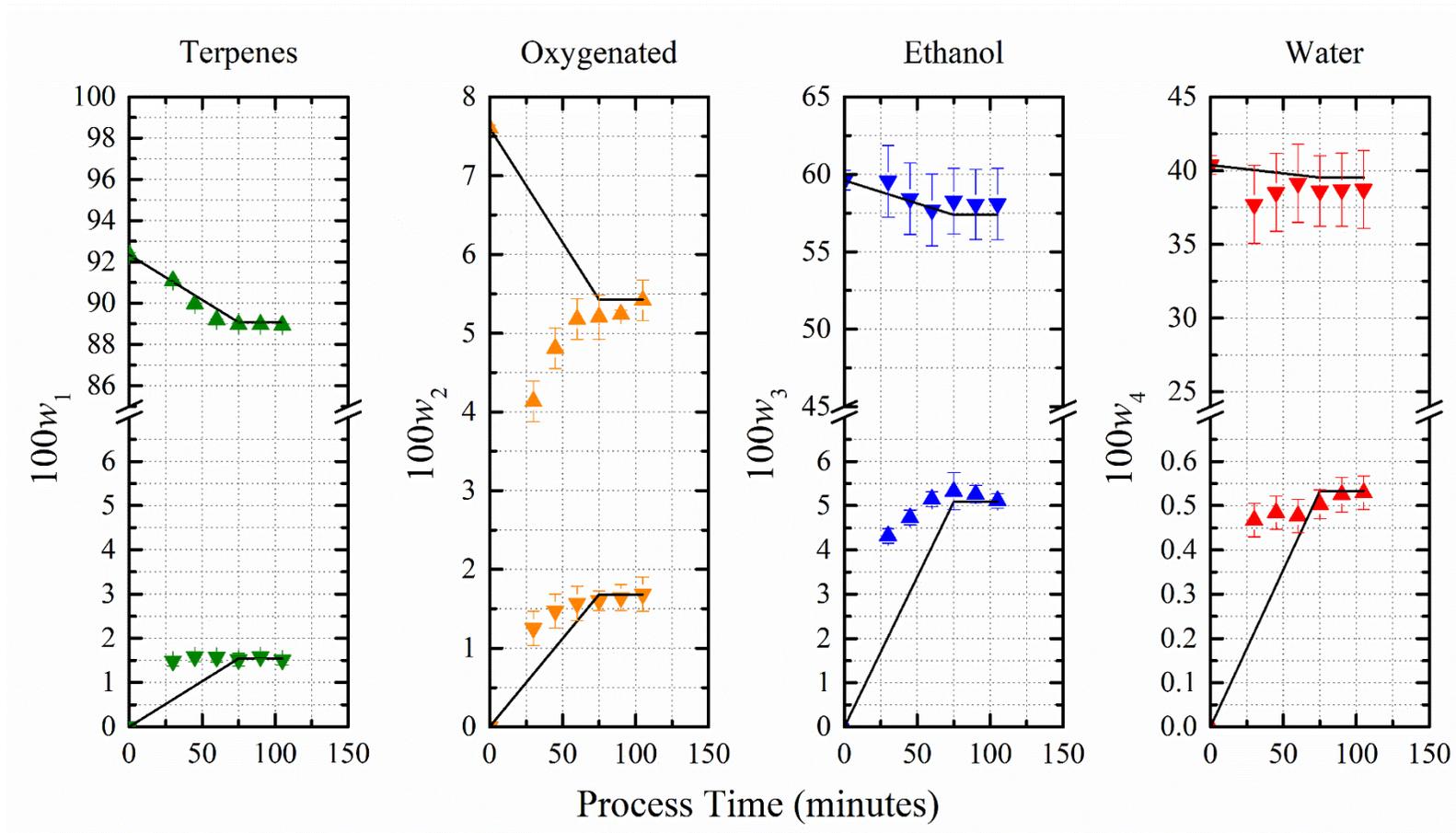


Figure A18: Composition profiles of the streams from the PRDC equipment, in mass percentage (100w), using ethanol + 40% (w/w) water as solvent. (1) terpenes; (2) oxygenated compounds; (3) ethanol; (4) water. (▲) raffinate stream; (▼), extract stream. The line (—) indicates the steady state.

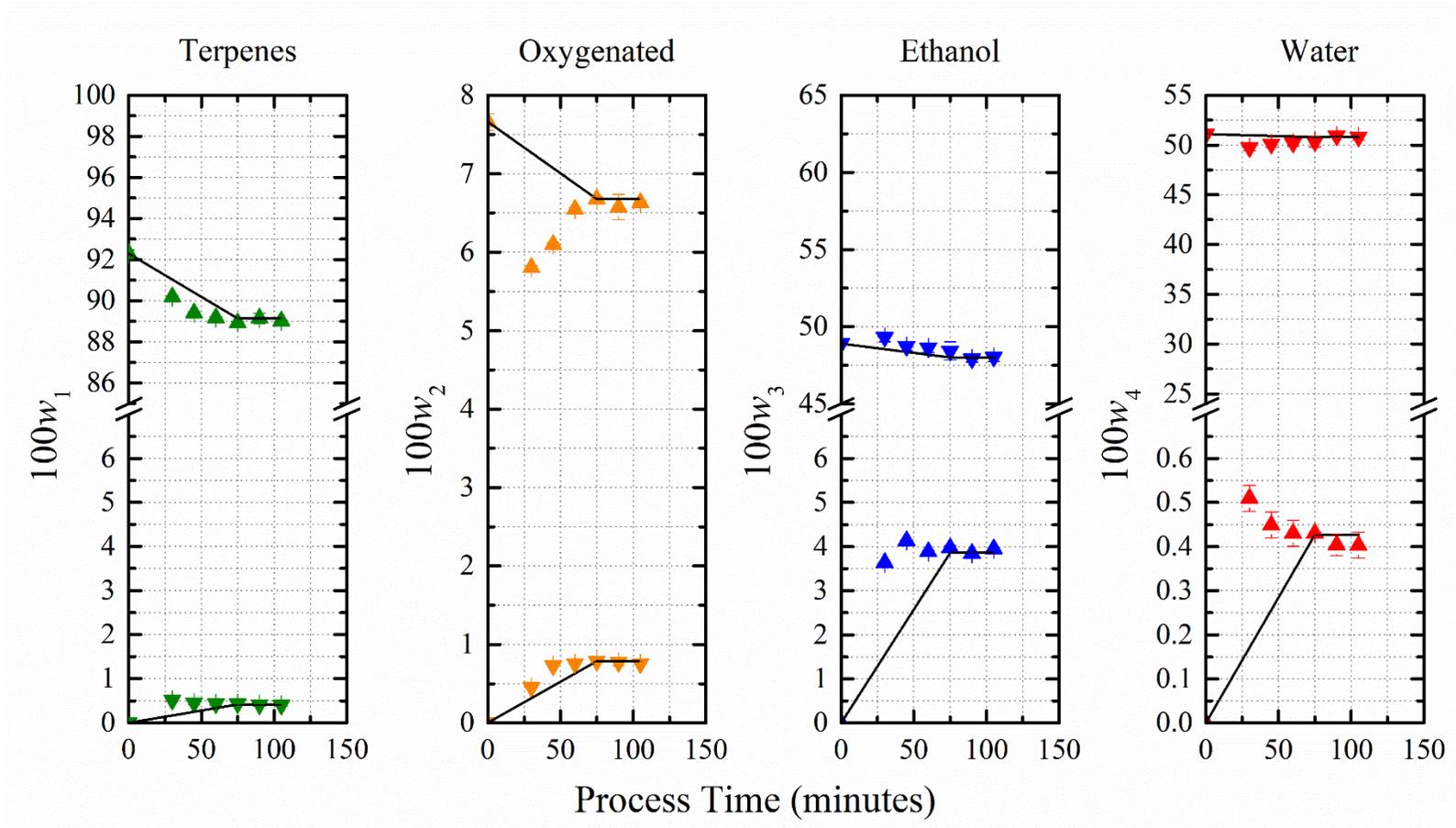


Figure A19: Composition profiles of the streams from the PRDC equipment, in mass percentage (100w), using ethanol + 50% (w/w) water as solvent. (1) terpenes; (2) oxygenated compounds; (3) ethanol; (4) water. (▲) raffinate stream; (▼), extract stream. The line (—) indicates the steady state.