Liquid-Liquid Equilibria for Ternary Systems Citronellal + Ethanol + Water and Citronellol + Ethanol + Water at 303.15 and 323.15 K

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ARTICLE INFO	ABSTRACT
Article history: Received 10 June 2023 Received in revised form 3 September 2023 Accepted 13 September 2023 Available online 30 September 2023 *Keywords:* Citronellal; Citronellol; Liquid-Liquid Equilibrium; NRTL; UNIQUAC	The liquid-liquid equilibria (LLE) for the ternary systems citronellal + ethanol + water and citronellol + ethanol + water are reported. The LLE of the systems have been measured at 303.15 and 323.15 K under atmospheric pressure as a reference for citronella oil production using solvent extraction method. The experimental data obtained were correlated using NRTL and UNIQUAC equations. The non-randomness parameter (α_{ij}) of the NRTL model is 0.2-0.47 and fits the experimental data satisfactorily. Both the NRTL and UNIQUAC models gave relatively good results for the systems investigated with the average Root Mean Square Deviation (RMSD) are 0.92% and 0.85% respectively. Based on the ternary diagram obtained in this work, it was found that the system followed the type I classification by Treybal. The binary interaction parameters generated in this study can also be used for LLE calculation in the design of extraction columns.

1. Introduction

Essential oils are one of the biggest commodities in Indonesia. Essential oils are produced from various kinds of plants from roots, branches, and other parts of a plant. One of the most widely produced essential oils in Indonesia is the citronella oil, which is obtained from the leaves and stems of different species of *Cymbopogon sp*. (lemongrass). Central Java province is the biggest producer of citronella oil, which is around 23.812 ton/year according to the Direktorat Jenderal Perkebunan Indonesia (Directorate General of Plantation Production Development) [1]. Citronella oil is widely used as room freshener, insect repellent, antifungal, and massage oil. It contains three main compounds called terpene, namely: geraniol, citronellal, and citronellol. Citronellal ($C_{10}H_{18}O$) is a monoterpenoid, the main component of citronella oil which gives lemon aroma and has a liquid form with a bright yellow color. Citronellol ($C_{10}H_{20}O$) is a kind of natural acyclic monoterpenoid that can be found in citronella oil and has a characteristic rose odor. Citronellol is slightly soluble in water and completely soluble in alcohol [2-4].

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The separation process of terpenes in essential oil is called deterpenation or fractionation. In industry nowadays, distillation is the most used method for the process. However, this method has disadvantages, such as the ability to degrade the oil, low yield, and not all impurities can be separated using this method. Currently, there are many studies on the separation of essential oil using solvent extraction method, it has become increasingly important in recent times due to the increasing demand for products that are thermo-sensitive, higher purity, and more efficient equipment used, this method is more acceptable because it doesn't need heating process [5]. Solvent extraction involves contact between the crude essential oil and the solvent, and yields raffinate phase which contains impurities like citronellyl acetate, geranyl acetate, etc, and extract phase which contains solvent and extracted solute (citronellal and citronellol) [6]. Therefore, this research is conducted to obtain a better separation process design for citronellal and citronellol. However, in carrying out solvent extraction method, supporting equilibrium data are needed, studies on solvent extraction techniques are limited by lack of data on the thermodynamic behavior of systems containing terpenes, oxygenated compounds, water, and solvent.

Similar researches on the use of solvent extraction to separate essential oils such as Fractionation of citrus essential oil by liquid-liquid extraction using a perforated rotating disc contactor, LLE of ternary system for - β citronellol in aqueous alcohol at different temperatures, Influence of the temperature on the (liquid + liquid) phase equilibria of (water + 1-propanol + linalool or geraniol), Liquid-Liquid Equilibria for Geraniol in Aqueous Alcohol Mixtures, Liquid + liquid equilibrium for systems composed of clove and allspice essential oil compounds and hydrous ethanol at T = 298.2 K, Liquid–Liquid Equilibria of Linalool + Ethanol + Water, Water + Ethanol + Limonene, and Limonene + Linalool + Water Systems, the influence of the temperature on the liquid-liquid equilibria of the mixture limonene + ethanol + H_2O, Liquid-Liquid Equilibria for the Ternary System Eugenol + Ethanol + Water at Temperatures 303.15, 313.15 and 323.15 K, Liquid-Liquid Equilibria for the Water + Ethanol + Citral and Water + Ethanol + Limonene Systems at 293 K and Liquid-liquid equilibria for quaternary system of eugenol + β-caryophyllene+ 1-propanol + water at temperatures 303.15, 313.15, and 323.15 K have been previously reported [7-16].

Solvent selection is important in solvent extraction method, in the future, solvents like ethanol and water are needed in food, cosmetic, and pharmaceutical industries. The light components in citronella oil are soluble in ethanol and slightly soluble in water. With, ethanol is chosen as solvent because of various reasons, such as it is very soluble in dilute solutions so that it can be used to make beverages and perfumes, it increases the aroma of the mixture, non-toxic, and affordable [17].

This research is conducted to obtain the liquid-liquid equilibrium data of ternary systems citronellal + ethanol + water and citronellol + ethanol + water at 303.15 and 323.15 K as the first step of the research of quaternary system and other systems that will be used as reference for the separation of terpenes from citronella essential oil using solvent extraction method.

2. Methodology
2.1 Experiment Using Equilibrium Cell

The components used were citronellal 95% and citronellol 97% from PT. Indesso Aroma, Ethanol from PT. Kurnia Jaya, and Aquadest. The experimental apparatus mainly consists of a 50 cm^3 equilibrium cell, a magnetic stirrer, a water bath along with a temperature regulator, and a water circulating pump to maintain a constant temperature.

This experiment was begun by mixing three components in the equilibrium cell. The first mixture, citronellal + ethanol + water, was mixed with certain composition using magnetic stirrer

while heated at a temperature that is maintained according to specified variable, 303.15 and 323.15 K at atmospheric pressure for 4 hours. After stirring, the mixture was settled for the next 20 hours to reach the equilibrium (total 24 hours for each sample), after the equilibrium was reached in each phase (organic phase and aqueous phase), then samples from each phase can be taken for Gas Chromatography (GC) analysis. This procedure then was done in other system, composition, and temperature variables.

2.2 Gas Chromatography Analysis

The citronellol, citronellal, and ethanol in organic and aqueous phase were analyzed using GC-FID (Flame Ionization Detector), with the inlet heating temperature of 250°C, using a split flow of 150 ml/min. The column used hydrogen gas with a purge flow of 5 ml/min, a gas saver flow of 10 ml/minute, and a gas saver time of 2 minutes. The duration of analysis for each sample is 15,667 minutes. Specifications on the detector use hydrogen gas 35 ml/minute, compressed water 350 ml/minute and make-up flow 40 ml/minute. While the water compositions in the organic and aqueous phase was determined by subtracting the sum of the other mole fractions from a value of 1 [18].

3. Results

The experimental data for the ternary mixtures of citronellal + ethanol + water and citronellol + ethanol + water at 303.15 and 323.15 K and atmospheric pressure are displayed in Table 1 and Table 2. All data are expressed in mole fractions. The experimental tie lines are also graphically presented in Figure 1 to Figure 8 for all temperatures investigated as straight (solid) lines. In these figures, two-phase regions were shown. The system exhibited type I phase behavior concurring to Treybal [19], which comprise of two pairs of completely miscible components (citronellal/citronellol + ethanol and ethanol + water) and one pair of partially miscible components (citronellal/citronellol + water). It can also be observed that the temperature has little effect on the LLE of this system. To assess the productivity of water in isolating ethanol from citronellal/citronellol, and they were calculated as Eq. (1) and Eq. (2).

$$D = \frac{w_{2\beta}}{w_{2\alpha}} \tag{1}$$

$$S = \frac{w_{2\beta}/w_{1\beta}}{w_{2\alpha}/w_{1\alpha}} \tag{2}$$

where $w_{2\alpha}$ and $w_{2\beta}$ are the concentrations of ethanol expressed in mass fraction within the organic and aqueous phases, individually. $w_{1\alpha}$ and $w_{1\beta}$ indicate the concentrations of citronellal/citronellol expressed in mass fraction within the over two phases, individually. D and S information at distinctive temperatures are listed in Table 1 and Table 2. From these tables and figures, it can be found that the distribution coefficients are inclined to diminish as the concentration of ethanol increments, when the system is stable. The selectivity portrays the adequacy of the extractant. As displayed in Table 1 and Table 2, the selectivity of the solvent is >1, uncovering the possibility of ethanol extraction utilizing water.

Table 1
LLE Data for the Citronellal (1) + Ethanol (2) + Water (3) System at 303.15 and 323.15 K and atmospheric pressure

| T[K]	Organic Phase			Aquoeus Phase			D	S
	x_1	x_2	x_3	x_1	x_2	x_3		
303.15	0.8802	0.0000	0.1198	0.0000	0.0000	1.0000		
	0.7506	0.0592	0.1901	0.0000	0.0207	0.9793	0.3493	12507.27
	0.7501	0.1309	0.1190	0.0000	0.0497	0.9502	0.3800	17453.75
	0.5963	0.1851	0.2187	0.0001	0.0710	0.9289	0.3839	2848.16
	0.5394	0.2220	0.2386	0.0000	0.0884	0.9116	0.3981	10093.59
	0.4477	0.2730	0.2794	0.0000	0.1142	0.8857	0.4185	8108.83
	0.3052	0.3637	0.3311	0.0001	0.1650	0.8349	0.4537	1559.60
	0.2909	0.3727	0.3363	0.0001	0.1676	0.8324	0.4496	1798.95
	0.1201	0.3437	0.5362	0.0015	0.2692	0.7293	0.7833	64.01
323.15	0.8086	0.0000	0.1780	0.0000	0.0000	1.0000		
	0.6802	0.1096	0.2102	0.0000	0.0498	0.9502	0.4547	309308.66
	0.5755	0.1593	0.2651	0.0000	0.0609	0.9391	0.3824	220076.38
	0.4738	0.2297	0.2965	0.0000	0.1127	0.8873	0.4907	232481.47
	0.3486	0.2805	0.3708	0.0000	0.1479	0.8521	0.5273	183838.92
	0.3034	0.3416	0.3550	0.0000	0.1700	0.8300	0.4976	150961.41
	0.1113	0.3156	0.5731	0.0027	0.2411	0.7561	0.7640	31.06
	0.2138	0.3360	0.4502	0.0004	0.2033	0.7963	0.6051	355.30

Table 2
LLE Data for the Citronellol (1) + Ethanol (2) + Water (3) System at 303.15 and 323.15 K and atmospheric pressure

| T [K]	Organic Phase			Aquoeus Phase			D	S
	x_1	x_2	x_3	x_1	x_2	x_3		
303.15	0.7597	0.0000	0.2403	0.0000	0.0000	1.0000		
	0.7057	0.1215	0.1728	0.0000	0.0320	0.9680	0.2635	13470.79
	0.5537	0.1665	0.2798	0.0000	0.0487	0.9512	0.2928	10042.48
	0.4992	0.2114	0.2895	0.0000	0.0642	0.9358	0.3038	7273.09
	0.4450	0.2459	0.3091	0.0000	0.0795	0.9205	0.3232	4259.47
	0.4034	0.3046	0.2920	0.0002	0.0964	0.9034	0.3164	648.64
	0.1162	0.3457	0.5381	0.0024	0.1920	0.8056	0.5555	27.35
	0.2850	0.3236	0.3913	0.0001	0.1000	0.8999	0.3091	990.28
323.15	0.6718	0.0000	0.3282	0.0000	0.0000	1.0000		
	0.5031	0.0948	0.4021	0.0001	0.0325	0.9675	0.3425	2445.98
	0.5001	0.1327	0.3673	0.0000	0.0422	0.9578	0.3179	18370.60
	0.4196	0.1675	0.4129	0.0000	0.0569	0.9430	0.3399	9036.97
	0.3749	0.2101	0.4151	0.0000	0.0766	0.9234	0.3644	4188.97
	0.3631	0.2155	0.4213	0.0000	0.0719	0.9281	0.3335	2575.32
	0.3202	0.2293	0.4505	0.0001	0.0866	0.9133	0.3778	2171.00
	0.1597	0.3495	0.4908	0.0013	0.1685	0.8302	0.4820	57.67
	0.1146	0.3720	0.5134	0.0039	0.1981	0.7980	0.5325	15.50
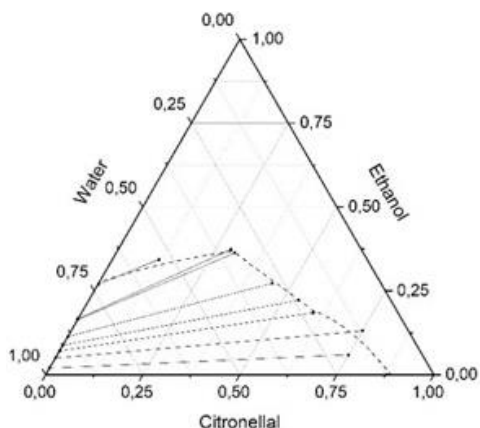
Fig. 1. Ternary phase diagram for the Citronellal (1) + Ethanol (2) + water (3) system at 303.15 K: (▪——▪) experimental data, (----) NRTL model
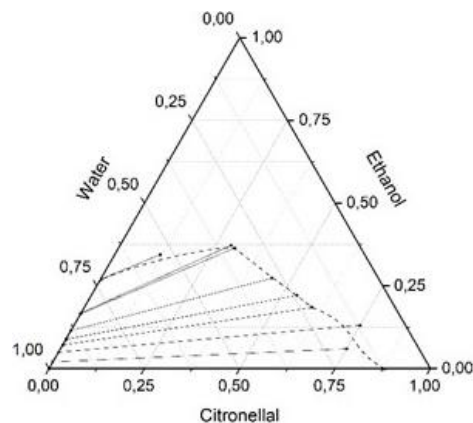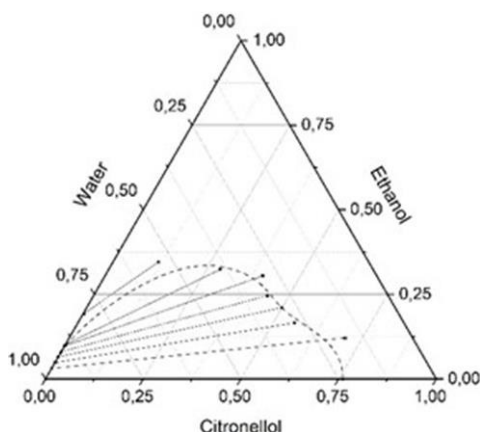

Fig. 2. Ternary phase diagram for the Citronellal (1) + Ethanol (2) + water (3) system at 303.15 K: (▪——▪) experimental (----) UNIQUAC model
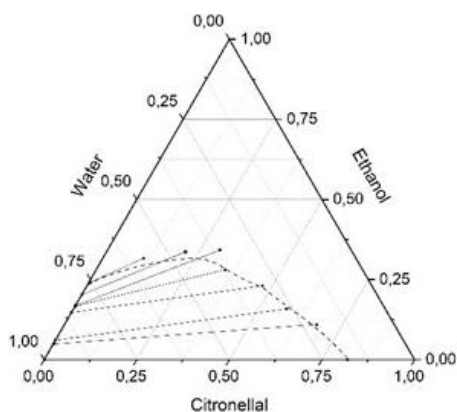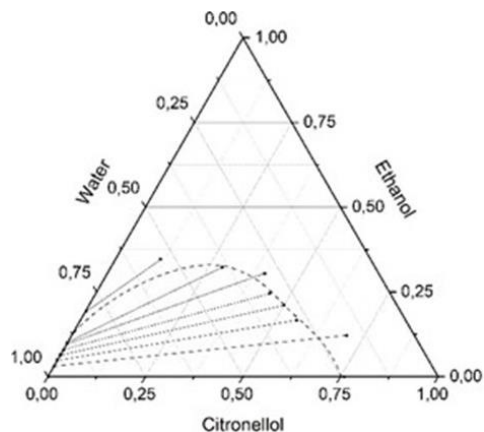

Fig. 3. Ternary phase diagram for the Citronellal (1) + Ethanol (2) + water (3) system at 323.15 K (▪——▪) experimental data, (----) NRTL model
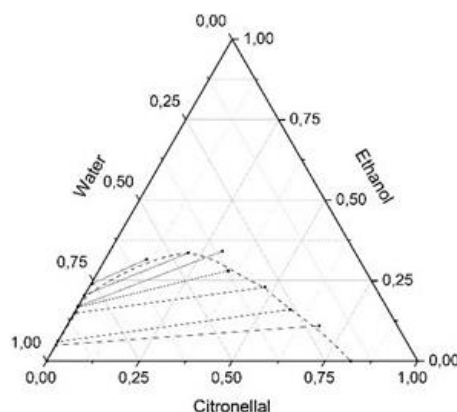
Fig. 4. Ternary phase diagram for the Citronellal (1) + Ethanol (2) + water (3) system at 323.15 K:(▪——▪) experimental data, (----) UNIQUAC model

Fig. 5. Ternary phase diagram for the Citronellol (1) + Ethanol (2) + water (3) system at 303.15 K (▪——▪) experimental data, (----) NRTL model

Fig. 6. Ternary phase diagram for the Citronellol (1) + Ethanol (2) + water (3) system at 303.15 K:(▪——▪) experimental data, (----) UNIQUAC model

Fig. 7. Ternary phase diagram for the Citronellol (1) + Ethanol (2) + water (3) system at 323.15 K:(■——■) experimental data, (----) NRTL model
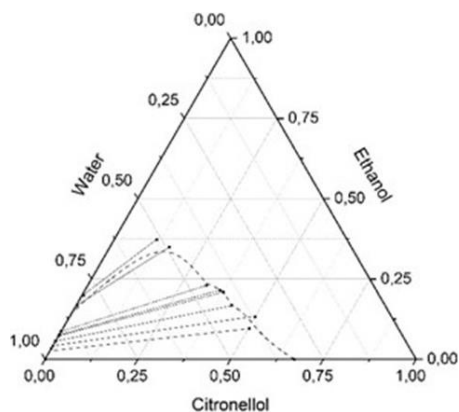
Fig. 8. Ternary phase diagram for the Citronellol (1) + Ethanol (2) + water (3) system at 323.15 K:(■——■) experimental data, (----) UNIQUAC model
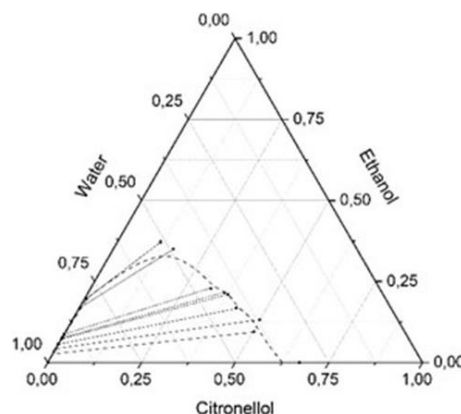
In this research, the LLE data were correlated using NRTL and UNIQUAC model to calculate the activity coefficients as presented in Eq. (3) and (4), respectively. NRTL and UNIQUAC thermodynamic models have been selected for correlation with the data because they were applicable for multicomponent and liquid-liquid equilibrium for essential oils [8,16,17]. Among them, the NRTL show can well represent numerous LLE systems by accurately selecting non-random parameters (α). In addition, non-random parameter α_{ij} of the NRTL show contains (α) esteem of from 0.2-0.47. For the UNIQUAC model, auxiliary parameters r and q of the pure components are taken from the Magnussen and listed in Table 3 [20].

$$ln\,\gamma_i = \frac{\sum_j^N \tau_{ji}G_{ji}x_j}{\sum_k^N G_{ki}x_k} + \sum_j^N \frac{x_j G_{ij}}{\sum_k^N G_{kj}x_k}\left(\tau_{ij} - \frac{\sum_k^N x_k \tau_{kj}G_{kj}}{\sum_k^N G_{kj}x_k}\right) \tag{3}$$

$$ln\,\gamma_i = ln\frac{\varphi_i}{x_i} + \frac{z}{2}q_i\,ln\frac{\theta_i}{\varphi_i} + l_i - \frac{\varphi_i}{x_i}\sum_j^N x_j l_i + q_i\left(1 - ln\sum_j^N \theta_j \tau_{ij} - \sum_j^N \frac{\theta_j \tau_{ij}}{\sum_k^N \theta_k \tau_{kj}}\right) \tag{4}$$

with

$$\varphi_i = \frac{r_i x_i}{\sum_k^N r_k x_k}; \theta_i = \frac{q_i x_i}{\sum_k^N q_k x_k}; l_i = \frac{z}{2}(r_i - q_i) + 1 - r_i \tag{5}$$

in which N shows the number of components, γ_i is the activity coefficient of component *i*, G_{ij} = exp(-$\alpha_{ij}\tau_{ij}$), G_{ji} = exp(-$\alpha_{ji}\tau_{ji}$), $\tau_{ii} = \tau_{jj} = 0$, $G_{ii} = G_{jj}$ =1, and $\alpha_{ij} = \alpha_{ji}$. The interaction parameters are defined as τ_{ij} = g_{ij}/T for NRTL and τ_{ij} = exp(g_{ij}/T) for UNIQUAC. The coordination number (z) of the UNIQUAC model is also set equal to 10 [21]. The binary interaction parameters (g_{ij} and g_{ji}) were defined by regressing the experimental LLE tie-line data show in Table 4 and Table 5 list the optimized values of binary interaction parameters of the NRTL and UNIQUAC models, respectively.

Table 3
UNIQUAC Structural Parameters (r and q)

Component	r	q
Citronellal	7.06	6.016
Citronellol	7.7364	6.808
Ethanol	2.5755	2.588
Water	0.92	1.4

The root-mean-square deviation (RMSD) used in used in this study was calculated based on the Eq. (6).

$$RMSD = \left\{ \sum_{K=1}^{n} \sum_{j=1}^{2} \sum_{i=1}^{3} \frac{(w_{ijk}^{exp} - w_{ijk}^{cal})^2}{6n} \right\}^{1/2} \tag{6}$$

where w^{exp} and w^{cal} represent the experimental mass fractions and values calculated by models, respectively. Subscripts i and j refer to the component and the phase, separately. Subscript k is the amount of tie lines, and n is the entire quantity of tie lines. The binary interaction parameter sets ($g_{ij} - g_{jj}$, $g_{ji} - g_{ii}$, $u_{ij} - u_{jj}$, and $u_{ij} - u_{jj}$) were gotten by minimizing the flowing objective function (OF) as in Eq. (7):

$$\boldsymbol{OF} = \sum_{K=1}^{n} \sum_{j=1}^{2} \sum_{i=1}^{3} (w_{ijk}^{exp} - w_{ijk}^{cal})^2 \tag{7}$$

The experimental data calculated through thermodynamic models UNIQUAC and NRTL for all systems studied are considered well-plotted in Figure 1 to Figure 8, affirming that both models are reasonable for recreating the extraction process of ethanol. The binary interaction parameter sets for NRTL and UNIQUAC models in conjunction with RMSD values for the studied systems from 303.15 to 323.15 K are shown in Table 4 and Table 5, and the RMSD values range from 0.57 % to 1.33 %. This demonstrate that both models are qualified to predict the LLE data for the studied systems.

Table 4
Binary Energy Parameters of NRTL and UNIQUAC Models for the Citronellal (1) + Ethanol (2) + Water (3) System

T [K]	Parameters	Composition (ij)	α	gij	gji	RMSD (%)
303.15	NRTL	1-2	0.47	493.08	5467.42	0.57%
		1-3		1674.41	12068.76	
		2-3		1950.15	1246.97	
	UNIQUAC	1-2	-	1053.19	609.90	0.70%
		1-3		1400.63	-212.90	
		2-3		827.19	1329.92	
323.15	NRTL	1-2	0.2	21.45	4771.43	0.83%
		1-3		1813.87	10160.02	
		2-3		9312.10	1850.90	
	UNIQUAC	1-2	-	64.00	-100.71	0.70%
		1-3		773.31	136.58	
		2-3		-156.36	145.37	

Table 5
Binary Energy Parameters of NRTL and UNIQUAC Models for the Citronellol (1) + Ethanol (2) + Water (3) System

T [K]	Parameters	Composition(ij)	α	gij	gji	RMSD (%)
303.15	NRTL	1-2	0.2322	2043.27	2510.27	0.93%
		1-3		6378.95	7033.94	
		2-3		5568.80	2846.02	
	UNIQUAC	1-2	-	71.84	70.09	1.05%
		1-3		530.39	418.50	
		2-3		104.29	144.64	
323.15	NRTL	1-2	0.2397	2044.42	2529.29	1.33%
		1-3		6395.20	7405.98	
		2-3		4189.58	2883.45	
	UNIQUAC	1-2	-	251.67	78.82	0.96%
		1-3		420.89	285.66	
		2-3		279.50	211.98	

4. Conclusions

Liquid-liquid equilibrium data of tie-line compositions were measured for the ternary mixtures of citronellal or citronellol + ethanol + water at 303.15 and 323.15 K under atmospheric pressure. The systems have a low solubility for citronellal and citronellol in the aqueous phase and a high solubility in the organic phase at any of the temperatures examined. The impact on temperature for the ternary LLEs represents the miscible region increment but the distribution ratios of alcohols rise as temperature increases. The experimental liquid-liquid equilibrium data were correlated using the NRTL and UNIQUAC activity coefficient models. The values (α_{ij}) of the NRTL model are 0.2-0.47. Both models gave relatively good results for the systems investigated, where the average rms deviations between the experimental results and those calculated by the NRTL and UNIQUAC models were 0.92% and 0.85% respectively. Based on the ternary diagram obtained in this work, it was found that the followed the type I classification by Treybal [19]. The binary interaction parameters generated in this study can also be used for LLE calculation in the design of extraction columns.

Acknowledgement

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