LIQUID-LIQUID EQUILIBRIA FOR THE SYSTEM COMPOSED BY WATER, ACETIC ACID, AND 1-HEXANOL AT 293.15 K AND UNDER ATMOSPHERIC PRESSURE USING REFRACTOMETRY AND DENSITOMETRY

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ABSTRACT – In order to evaluate the accuracy of an indirect quantification method, the liquid-liquid equilibrium for the ternary system composed by water, acetic acid and 1-hexanol at 293.15 K and at atmospheric pressure was determined by means of refractometry and densitometry. The binodal curve was measured using the cloud point method, while the tie-lines were obtained in a cell-glass where the mixture was vigorously stirred and maintained at constant temperature. After the completeness of phase separation, samples were collected using simple syringe needles and the concentration of all components were satisfactorily obtained using the relation between the refraction index and density with the binodal curve sample concentrations. Generated data were correlated using NRTL model, and their quality were verified by Othmer-Tobias and Hand tests. All the results were compared with a previous work which quantified the equilibrium phases by means of a direct method (gas-chromatographic analysis). The indirect method were very efficient, resulting in two equations that related the physical properties with sample concentrations with an average relative deviations between the experimental and calculated physical properties lower than 0.01%. NRTL model parameters were regressed and the mean deviation was 0.61. Othmer-Tobias and Hand tests presented coefficients of determination of 0.9984 and 0.9975, indicating the high quality of these data.

1. INTRODUCTION

In order to separate a component of interest from a liquid mixture, the liquid extraction technique is widely used by the chemical industry. This type of separation is present in various processes, such as the removal of high boiling organic compounds from wastewater, product recovery from reactions, in the refining of oils and in solvent concentration (Kubota and Masahiro, 2006; Stoicescu *et al.*, 2008; Rodrigues *et al.*, 2007; Liu *et al.*, 2014; Senol, 2013). In order to design a liquid extractor equipment and to optimize the separation process, the solubility behavior of the mixture components must be known precisely, and the thermodynamic modeling of the system must be determined (Lo and Baird, 2001; Juang *et al.*,

1997). One of the step of these procedures is the quantification of the extracted and refined phases. With these data, it is possible to determine some process factors, such as the solvent selectivity and the partition coefficient (Geankoplis, 2003; Stevens *et al.*, 2007). Usually, direct methods are used to obtain the concentrations of the phases in equilibrium, like gas chromatography. When direct methods are expansive, concentrations can be determined by indirect methods. In the case of liquid-liquid equilibria, by correlating the concentration of each component in a mixture that lies on the binodal curve with a chemical or physical property, one can posteriorly obtain the concentration of the extracted and refined phases in equilibrium. This procedure is widely used in quantification for a variety of systems, like polymers, ionic liquids, methyl esters, alcoholic systems and so on (Almeida *et al.*, 2012; Batistell *et al.*, 2011; Taha *et al.*, 2012; Rocha *et al.*, 2014). In general, as differences among pure component properties increase, accuracy of the indirect method increases. Calibration curves of some properties like refraction index, density, speed of sound, spectrophotometry, viscosity and others, can be related with mass concentration of the samples obtained at the binodal curve by the cloud point method.

This paper aimed to compare the phase quantification between indirect methods, i.e., refractometry and densitometry, with a direct method, i.e., gas chromatography (Senol, 2004). For this purpose, binodal curve was determined through the cloud point method and related with the two physical properties investigated in this study. The tie-line data were modelled using NRTL model (Renon and Prausnitz, 1968), and their quality were verified by Othmer-Tobias (Othmer and Tobias, 1942) and Hand (Hand, 1930) tests.

2. MATERIALS AND METHODS

2.2 Materials

Acetic acid was purchased from Sigma Aldrich with a purity of 99.7 %. 1-Hexanol was also provided by Sigma Aldrich and presented 99 % of purity. Distilled water was used in the experiments. Table 1 presents the physical properties density (ρ) and refraction index (nD) of the components measured using a refractometer (RE 40D, Mettler-Toledo) and a densimeter (DMA 5000, Anton Paar), at the temperature of experiments (293.15 K) and at the temperature of the calibration curves (298.15 K). Note that the differences among measured values at these two temperatures for each compound were lower than 0.5 %.

Table 1 – Physical properties (density and refraction index), at 293.15 and 298.15 for the pure components.

Component	$\rho^{293.15°C}$ [g/cm^3]	nD$^{293.15°C}$	$\rho^{298.15°C}$ [g/cm^3]	nD$^{298.15°C}$
1: Water	0.99821	1.3325	0.99708	1.3300
2: Acetic Acid	1.05127	1.3724	1.04566	1.3703
3: 1-Hexanol	0.81860	1.4180	0.81506	1.4161

2.3 Experimental procedure

2.3.1 Binodal curve and calibration curves

The binodal curve was determined by the cloud point method. In a cell glass, homogeneous binary systems (water/ acetic acid and ethanol/ acetic acid) of known mass concentrations were prepared using an analytical balance (AS 220/C/2, Radwag), accurate to 0.0001g, and stirred vigorously using a magnetic stirrer. System temperature was maintained constant at 293.15 ± 0.1 K with a thermostatic bath (Viscotherm VT2, Anton Paar GmbH). The third component was added in the solution using an automatic burette (Dosimat 715, Metrohm) until the system turbidity occurred. Then, for each drop of the third compound added, the mixture remained stirring for approximately five minutes, and then agitation was paused allowing the transparency/turbidity identification. At this time, a cloudy sample was collected and injected using simple syringes in the refractometer and in the densimeter subsequently. Each sample was analyzed in triplicates at 298.15 K, i.e., 5 K above the equilibrium temperature, to ensure that sample was homogeneous and isotropic. In this way, phase splitting was avoided during measurements in the refractometer and densimeter. Calibration curves at 298.15 K are commonly used for quantification of isobaric vapor-liquid equilibria (Yu *et al.*, 2000).

2.3.2. Tie-lines measurement and thermodynamic correlation

Tie-lines were measured by preparing mixtures with mass concentration within the diagram region delimited by the binodal curve, to ensure phase split. Ternary mixtures were agitated vigorously with a magnetic stirrer for 3 hours in an equilibrium glass cell. Then, the system rested for a period of 12 hours, allowing the completeness of the phase split, regarded by a clean and well defined phase boundary between the phases. Samples were collected using syringes and analyzed in the densimeter and the refractometer.

Generated data for the tie lines in terms of concentrations of each compounds in the two phases in equilibrium were adjusted using the NRTL model. Equation 1 presents the relation between the activity coefficient of component *i* with its mass concentration on the phase α presented by NRTL model.

$$\ln \gamma_i^{\alpha} = \frac{\sum_{j}^{C} \tau_{ji} G_{ji} x_j}{\sum_{k}^{C} G_{ki} x_k} + \sum_{j=1}^{C} \left[\frac{x_j G_{ij}}{\sum_{k}^{n} G_{kj} x_k} \left(\tau_{ij} - \frac{\sum_{r}^{C} \tau_{ri} G_{rj} x_k}{\sum_{k}^{C} G_{kj} x_k} \right) \right] \tag{1}$$

$$G_{ij} = \exp\left(-\alpha_{ij} \tau_{ij}\right) \tag{2}$$

$$\tau_{ij} = \frac{A_{ij}}{T} \tag{3}$$

$$\alpha_{ij} = \alpha_{ji} \tag{4}$$

where: γ_i^α: activity coefficient of component i in phase α; x: molar fraction; A_{ij} e A_{ji}: adjustable parameters to the experimental data; α_{ij} e α_{ji}: parameter of the non randomness of the mixture.

The mean deviation between the experimental and calculated compositions were determined through Equation 5.

$$\delta x = 100 \sqrt{\frac{\sum_i^M \sum_j^N \left\{ \left(x_{ijk}^{I,exp} - x_{ijk}^{I,calc}\right)^2 + \left(x_{ijk}^{II,exp} - x_{ijk}^{II,calc}\right)^2 \right\}}{2MN}} \tag{5}$$

where: M: number of tie-lines; N: number of components.

3. RESULTS

3.1. Binodal curve and calibration curves

Table 2 presents the experimental data for cloud points for the system water (1), acetic acid (2) and 1-hexanol (3) at 293.15 K. The refraction indexes and densities of the binodal curve mixtures measured at 298.15 K are also shown.

Table 2 – Cloud point for the aqueous and organic phase at 293.15 K, refraction index and density at 298.15 K.

Aqueous Phase						Organic Phase					
$100w_1$	$100w_2$	nD	σ ($\times10^5$)	ρ [g/cm³]	σ^a ($\times10^5$)	$100w_1$	$100w_2$	nD	σ^a ($\times10^5$)	ρ [g/cm³]	σ^a ($\times10^5$)
99.15	0.00	1.3332	0.000	0.99735	8.340	6.57	0.00	1.4098	4.71	0.83026	8.219
96.15	2.97	1.3349	0.000	1.00127	4.546	7.08	2.02	1.4087	0.00	0.83458	26.242
90.15	8.89	1.3389	0.000	1.00961	5.354	7.79	6.30	1.4065	0.00	0.84456	9.031
85.53	13.46	1.3414	4.714	1.01486	8.957	9.33	10.12	1.4045	4.71	0.85475	10.339
78.97	19.87	1.3458	0.000	1.02245	7.040	11.17	15.83	1.4014	4.71	0.86882	9.393
70.01	28.34	1.3513	0.000	1.03187	9.092	14.64	22.90	1.3974	0.00	0.88876	18.409
64.87	33.13	1.3562	4.714	1.03736	5.735	17.35	27.28	1.3948	4.71	0.90234	8.042
57.60	37.41	1.3603	0.000	1.04272	7.789	22.04	32.05	1.3910	4.71	0.92040	13.736
52.18	40.12	1.3641	4.714	1.04635	16.540	27.91	35.15	1.3872	0.00	0.93766	18.373
43.91	42.02	1.3687	0.000	1.04845	14.197	32.57	38.01	1.3839	4.71	0.95149	16.310

[a]σ = standard deviation among triplicates for the physical properties.

Relationships between the concentrations of each compound in the mixture and the physical properties shown in Table 2 were adjusted with a linear function or a second order polynomial. By analyzing the better coefficients of determination among these correlations, water and acetic acid were selected. Then two quadratic functions (Equations 6 and 7) were generated for relating density and refraction index with the mass concentration of water (w_1) and acetic acid (w_2), according to Rocha (2014).

$$nD = 1.4062 + 0.0647w_1 - 0.14w_1{}^2 - 0.056w_2 + 0.0123w_2{}^2 - 0.0823w_1w_2 \quad (6)$$

$$\rho = 0.8978 - 1.0803w_1 + 1.197w_1{}^2 + 0.3014w_2 + 0.3923w_2{}^2 + 0.961w_1w_2 \quad (7)$$

The equations 6 and 7 presented an average relative deviation of 0.036 and 0.48% for the refraction index and density functions, respectively, and their coefficient of determination were 0.9996 and 0.996. These two equations were used to quantify concentration of the extract and raffinate phases in the tie-line measurement.

3.2 Tie-lines measurement and thermodynamic modelling

To obtain the tie-lines, six samples with their mass concentrations within the binodal curve were prepared, and after phase splitting, refraction index and the density were measured for each phase. The measured values of each physical property was equaled to Equations 6 and 7, and the mass concentrations of water and acetic acid calculated. Mass concentration of 1-hexanol was obtained by difference. Table 3 presents the overall concentration, the physical properties of the two phases and their standard deviations, as well as the concentrations calculated by the indirect method.

Table 3 – Overall composition of the mixture, physical properties of the aqueous and organic phase with their mass fraction determined by equation 3 and 4.

Overall composition		Aqueous Phase						Organic Phase					
$100w_1{}^a$	$100w_2{}^a$	nD	σ ($\times10^5$)	ρ [g/cm³]	σ ($\times10^5$)	$100w_1{}^a$	$100w_2{}^a$	nD	σ ($\times10^5$)	ρ [g/cm³]	σ ($\times10^5$)	$100w_1{}^a$	$100w_2{}^a$
45.03	5.04	1.3374	0.000	1.00616	8.287	92.15	7.19	1.4072	4.714	0.84074	5.099	7.79	5.01
40.22	10.01	1.3401	4.714	1.011347	13.888	87.80	11.70	1.4052	4.714	0.84543	5.793	9.65	9.45
35.28	14.95	1.3442	4.714	1.018913	6.549	81.46	17.91	1.4022	4.714	0.85633	8.731	12.13	15.08
30.18	19.98	1.3480	4.714	1.025537	24.513	75.73	23.15	1.3995	0.000	0.87136	18.385	14.06	19.79
25.03	25.04	1.3525	0.000	1.034157	6.799	68.95	28.96	1.3968	4.714	0.89152	28.004	15.40	24.19
43.27	32.33	1.3576	4.714	1.040267	9.534	61.59	34.40	1.3932	0.000	0.91348	22.226	19.06	29.64

[a]: water (w_1) and acetic acid (w_2)

Data shown in Table 3 were correlated with NRTL model using an algorithm based on maximum likelihood proposed by Stragevitch and D´Avila (1997). The regressed parameters are presented in Table 4.

Table 4 – Regressed parameters for NRTL model for water (1), acetic acid (2) and 1-hexanol (3) at 293.15K.

Pair	Aij/K	Aji/K	αij
12	-0.18091	-257.99	0.21918
13	2094.0	124.75	0.25258
23	113.83	-656.16	0.34000

Experimental data for binodal curve and tie-lines together with NRTL model are presented in Figure 1. It is also shown experimental data from Senol (2004).
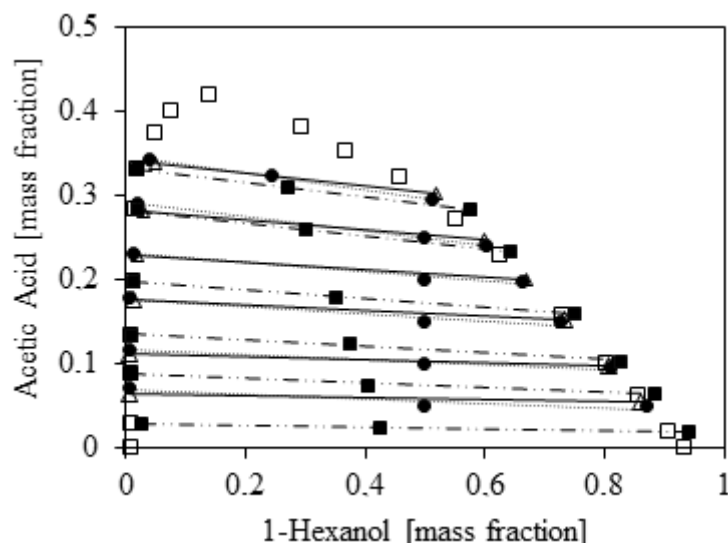
Figure 1 – Phase equilibrium diagram of the system water (1), acetic acid (2) and 1-hexanol (3) at 293.15 K. Legend: ○ binodal curve; (●——) experimental tie-lines; (Δ …) NRTL tie-lines; (■ –··–) experimental tie-lines from Senol (2004).

As can be observed in Figure 1, the indirect quantification of the ternary system showed accurate concentration for both aqueous and organic phases, since the filled black points coincided with the binodal curve. Also, it is possible to verify that the NRTL model satisfactorily correlated the experimental data, resulting in a mean deviation of 0.61 %. From Figure 1, one can compare the results obtained from the direct method with those obtained in this study, and it is possible to verify that the indirect method presented a more precise result than the quantification accomplished through gas chromatography.

In order to verify the quality of data presented in this work, mass concentrations in both phases were related by the Othmer-Tobias and Hand tests. Figure 2 shows the linear correlations obtained.
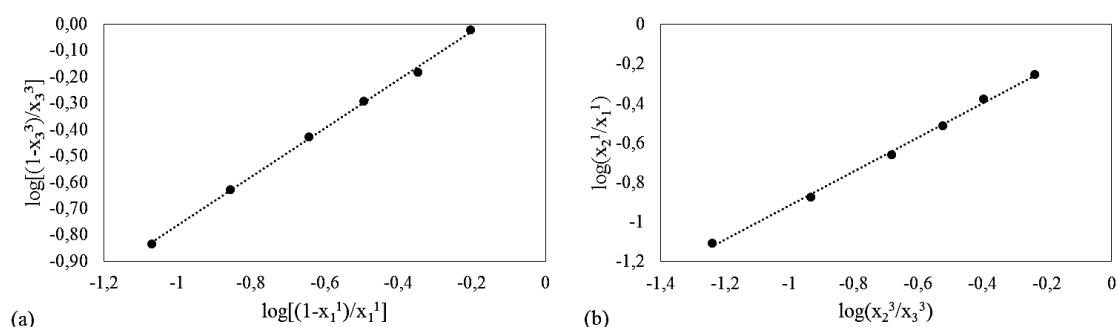

Figure 2 – Quality tests for water (1), acetic acid (2) and 1-hexanol (3): (a) Othmer-Tobias method; (b) Hand method. Legend: x_i^j: molar fraction of component i present in the phase rich in component j.

Figure 2 indicates that the experimental data obtained for the system using the indirect method have a very good quality, with coefficients of determination of 0.9984 and 0.9975 for the Othmer-Tobias and Hand tests, respectively.

4. CONCLUSION

The liquid-liquid equilibrium data for the system water, acetic acid and 1-hexanol at 293.15 K and under atmospheric pressure was determined using densimetry and refractometry. The system binodal curve were measured using the cloud point method and the physical properties were correlated with the mass concentrations of the cloudy samples, enabling the quantification of the extract and raffinate phase in the tie-lines measurement. The quantification of the equilibrium phases was satisfactorily obtained using the indirect method, which presented two equations that predicted very well the compositions of the equilibrium phases. The data were precisely correlated by the NRTL model, presenting a mean deviation of 0.61. The Othmer-Tobias and Hand tests showed high quality data.

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