Measurements and correlation of liquid–liquid equilibrium of Water + Carboxylic Acid or Alcohol + 1,8-Cineole ternary systems

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Abstract

Liquid-liquid equilibrium data are presented for mixtures of (water (1) + propionic acid, or propanol (2) + 1,8-cineole (3)) at T = 291.15 K and P = 1 atm. The ternary systems exhibit type-1 behavior of LLE. The tie-line data were correlated using the NRTL model. Moreover, the binary interaction parameters of this model were obtained by minimizing well defined objective functions using the Genetic Algorithm (GA) and the Particle Swarm Optimization (PSO). In addition, the reliability of the experimental tie-line data was determined through the Othmer–Tobias and Hand plots. Finally, Distribution coefficients (D) and separation factors (S) were calculated to evaluate the capability of solvent for separation of acid or alcohol from water.

Keywords: Liquid-liquid equilibrium; 1, 8-cineole; Genetic Algorithm (GA); Particle Swarm Optimization (PSO).

I.   Introduction

The determination of accurate phase equilibrium data for multicomponent mixtures has paramount importance to the study of various chemical processes. For example, good design of an extraction equipment requires experimental determination and/or theoretical prediction of liquid–liquid equilibrium (LLE) data. In recent years, several authors [1–8] have investigated LLE of ternary systems.

The efficient separation of carboxylic acids and alcohols from aqueous solutions is an important concept in the chemical fermentation industry. Liquid–liquid extraction could be an alternative method to separate the carboxylic acid or alcohol + water mixture. The key of the process is the use of an appropriate solvent in order to achieve the mixture separation. The solvent must be cheap and their recovery process easily to be implanted in order to minimize costs and environmental problems. Moreover, a solvent with these characteristics could make extraction process economically viable versus other alternatives [9]. Eucalyptus oil and its main component, 1,8-cineole, have been investigated as potential co-solvents. This study formed one aspect of utilizing solar energy stored in plants as liquid fuel components [10]. The LLE data of the ternary systems (water + propionic acid or propanol + 1,8-cineole) are reported at $T = 291.15$ K and 1 atm. Then, the solubility and tie line data for these systems, determined by using the cloud-point method, are presented. This technique provides the concentration of all components in the mutually saturated liquid phases [11, 6]. The quality of the experimental tie line data will be confirmed by the Othmer-Tobias [12] and the Hand [13] correlations on a mass-fraction basis. The tie-line data were correlated using the non-random two-liquid (NRTL) [14] model. For this purpose, two evolutionary optimization techniques were used: the genetic algorithm (GA)and the particle swarm optimization (PSO) method, in order to estimate the binary interaction parameters of the NTR model.

II. Experimental

A. Materials

The purity of the chemical species employed in this work and their origin were as follows: Propionic acid (Merck, >99%), propanol (Biochem, >98%), 1,8-cineole, >95%(GC). These chemical compounds were used without further purification. Deionized and redistilled water was employed throughout all experiments.

B. Apparatus and procedure

The solubility curve for the ternary systems were determined by the cloud point method [15] using a thermostated cell, equipped with a magnetic stirrer and an isothermal fluid jacket. The cell temperature was measured within an accuracy of ±0.2 K using a mercury-in-glass thermometer. The end-point was determined by observing the transition from a homogeneous to a heterogeneous mixture. For the water-rich and solvent-rich phases, (1) binary mixtures of (water + solute (propionic acid, or propanol)) were titrated with 1,8-cineole, and (2) binary mixtures of (1,8-cineole + solute (propionic acid, or propanol)) were titrated with water, until the transition from homogeneity to cloudiness was observed. All these titrations involved refractive index measurements using a Nahita Model 690/1 refractometer. All mixtures were prepared by weighing with an analytical balance (model Nahita 5034/200, accurate to ± 0.0001 g).

The tie-line data were determined by a magnetically stirred equilibrium cell, which was kept in a constant-temperature bath for two hours, maintained at (291.15 ± 0.2K). The prepared mixtures were left to settle for 24 hours for separation into two clear phases at equilibrium. After that, samples from both organic and aqueous phases had been taken using a syringe (2 ml) for analysis.

III. Results and discussion

A. Experimental solubility and tie line data

The tie line data of the (water +propionic acid + 1, 8-cineole) and (water +propanol+ 1, 8-cineole) ternary systems, obtained experimentally at T = 291.15 K and 1 atm, are given in Tab. 1, where x_{i1} and x_{i2} refer to the mass fractions of the ith component in aqueous and organic phases, respectively. The solubility curves and tie lines data are plotted in Fig. 1-2. Because (solute+ water) and (solute + 1, 8-cineole) are two liquid pairs that are completely miscible and the only liquid pair (water + 1,8-cineole) is partially miscible, these ternary systems behave as type-1 LLE [16].

Table 1. Experimental tie-line results in mass fraction for ternary systems.

Water-rich phase (aqueous phase)			Solvent-rich phase (organic phase)		
X_1	X_2	X_3	X_1	X_2	X_3
Water (1) + Propanol (2) +1,8-cineole (3)					
0.0043	0.0686	0.9271	0.9697	0.0301	0.0020
0.0046	0.1249	0.8705	0.9235	0.0709	0.0056
0.0046	0.1617	0.8337	0.8827	0.1075	0.0098
0.0038	0.2142	0.7820	0.8641	0.1256	0.0103
0.8171	0.1703	0.0126	0.0025	0.2664	0.7311
Water (1) + Propionic acid (2) +1,8-cineole (3)					
0.8369	0.1573	0.0058	0.0054	0.0615	0.9331
0.7571	0.2366	0.0063	0.0082	0.1006	0.8912
0.6456	0.3503	0.0041	0.0099	0.1314	0.8587
0.5539	0.4407	0.0054	0.0110	0.1476	0.8414
0.4776	0.5144	0.0080	0.0121	0.1645	0.8234

B. LLE correlation and parameter estimation

The NRTL model [14] was chosen to correlate the experimental data of the tie-lines. The non-randomness parameter in the NRTL model (α) was set equal to 0.2 as usual in order to reduce the dimensions of the optimization search domain. In addition, Fig. 1-2 compares the results between the calculated and experimental tie lines. It is evident that the NRTL model can predict well the experimental behavior of the tie-lines. In Tab.4, the interaction binary parameters of the NRTL model, using the two proposed optimization algorithms (GA and PSO), are presented along with the model prediction error. This error was computed based on the root-mean square deviation (RMSD).

The above optimization problem was formulated so that an advantage was taken of the closure equation that related the six binary interaction parameters as follows [5]:

$$A_{12} - A_{21} + A_{23} - A_{32} + A_{31} - A_{13} = 0 \qquad (1)$$

Thus, only five out of six binary interaction parameters were independent and needed to be determined by our evolutionary algorithms.
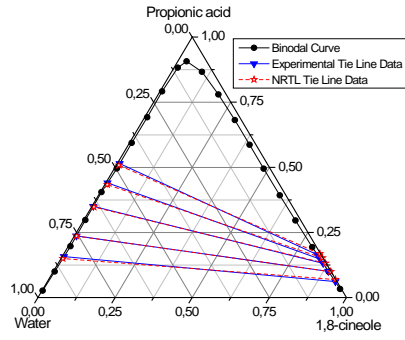
Figure 1. LLE ternary diagram for water (1) +propionic acid (2) + 1,8-cineole (3) at 291.15 K.
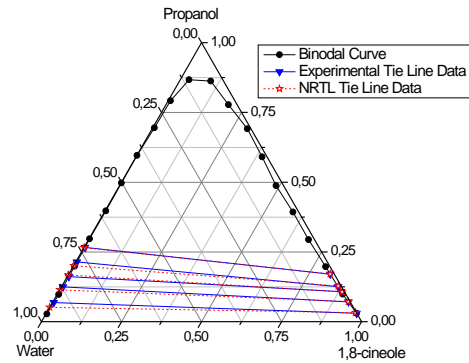

Figure 2. LLE ternary diagram for water (1) +propanol (2) + 1,8-cineole (3) at 291.15 K.

In order to compare the results obtained by the GA and PSO, the error was measured based on the Root Mean Squared Deviation (RMSD) between the computed (using the NRTL model) and experimental mass fractions using the following expression:

$$\text{RMSD} = \sqrt{\frac{\sum_{k=1}^{n}\sum_{j=1}^{2}\sum_{i=1}^{3}(x_{ijk}^{exp} - x_{ijk}^{cal})^2}{6n}} \qquad (2)$$

where x_{ijk}^{exp} is the experimental mass fraction of the tie line, x_{ijk}^{cal} is the calculated mass fraction of the tie line, $k = 1, 2,…, n$ (tie line), j is the aqueous or organic phase and i is the number of components.

C. Distribution coefficient and separation factor

The distribution coefficients, d_i, for water ($i=1$) and solute (PA or propanol) ($i=2$), and the separation factors, S, were calculated as follows [7]:

$$d_i = \frac{x_{i3}}{x_{i1}} \qquad (3)$$

$$S = \frac{d_2}{d_1} = \frac{x_{23}/x_{21}}{x_{13}/x_{11}} \qquad (4)$$

where x_{13} and x_{23} are the mass fractions of water and solute in organic phase, respectively, while x_{11} and x_{21} are the mass fractions of water and solute in aqueous phase, respectively.

The distribution coefficients and separation factors for the ternary systems at T= 291.15K are given in Tab. 2.

Table 2. Distribution coefficients of water (d_1) and PA or propanol (d_2) and separation factors (S) at 291.15 K.

d_1	d_2	S
Water(1) + Propanol(2) + 1,8-cineole(3)		
0.0032	0.4388	137.13
0.0064	0.5676	88.69
0.0117	0.6648	56.82
0.0132	0.5864	44.42
0.0172	0.6393	37.17
0.0222	0.6824	30.74
Water(1) + Propionic acid(2) + 1,8-cineole(3)		
0.0065	0.3909	60.59
0.0108	0.4252	39.26
0.0153	0.3751	24.46
0.0199	0.3349	16.86
0.0253	0.3198	12.62

It is apparent from the distribution coefficients and separation factors data that the separation of propionic acid and propanol from water by extraction with 1, 8-cineole was feasible.

On the other hand, the separation factors are shown in Fig. 3 as function of the solute composition in the aqueous phase.
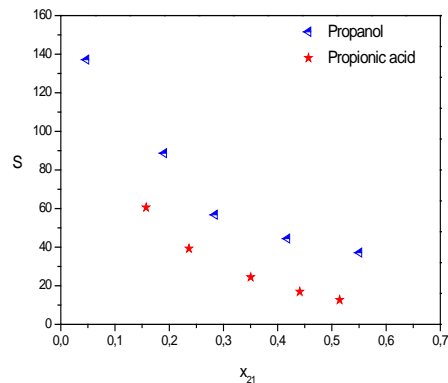

Figure 3. Separation factors (S) of (water + solute (PA or propanol) + 1,8-cineole) as a function of mass fraction of solute in the aqueous phase x_{21} at 291.15 K.

D. Othmer-Tobias and Hand correlations

The reliability of the experimental tie-line was ascertained by applying the Othmer-Tobias [12] and the Hand [13] correlations as shown in Eq. (5) and Eq. (6) respectively:

$$\ln\left[\frac{1-x_{33}}{x_{33}}\right] = a_1 + b_1 \ln\left[\frac{1-x_{11}}{x_{11}}\right] \qquad (5)$$

$$\ln\left[\frac{x_{21}}{x_{11}}\right] = a_2 + b_2 \ln\left[\frac{x_{23}}{x_{33}}\right] \qquad (6)$$

Where x_{11} and x_{21} are the mass fractions of water and solute in aqueous phase, respectively, x_{23} and x_{33}, are the mass fractions of solute and 1, 8-cineole in organic phase, respectively, a_1, b_1, a_2 and b_2 are the parameters of the Othmer-Tobias and the Hand correlations, respectively. The parameters of the correlations are listed in Tab. 3.

Table 3. Constants of Othmer–Tobias and Hand correlations for the water + PA or propanol + 1, 8-cineole ternary system at 291.15 K.

Corrélations	
Othmer-Tobias	**Hand**
Water (1) +Propanol (2) +1,8-cineole (3)	
a_1 = 0.0371	a_2 = 0.1040
b_1 = 0.7742	b_2 = 0.8321
R^2 = 0.9669	R^2 = 0.9750
Water (1) +Propionic acid (2) +1,8-cineole (3)	
a_1 =-1.5222	a_2 = 2.4306
b_1 =0.6117	b_2 = 1.5553
R^2 =0.9328	R^2 = 0.9355

Table 4. NRTL (α = 0.2) binary interaction parameters (Aij and Aji) and root-mean square deviation (RMSD) values for the (Water + PA or propanol + 1,8-cineole) ternary system.

Systems	i-j	GA	PSO	RMSD (%)	
		$A_{ij}10^3$	$A_{ij}10^3$	GA	PSO
Water +propanol+ 1,8-cineole	1-2	-0.7339	-1.1560	**0.80**	**0.52**
	1-3	0.9493	0.9343		
	2-3	-0.1328	0.7035		
	2-1	0.6612	0.9043		
	3-1	3.0587	0.9897		
	3-2	0.2882	-1.3014		
Water + PA + 1,8-cineole	1-2	-0.1130	-0.0735	**0.54**	**0.29**
	1-3	0.1281	1.1455		
	2-3	0.4428	0.9775		
	2-1	0.3851	0.6253		
	3-1	2.3952	0.9350		
	3-2	0.1327	0.0682		

According to the results reported in Tab.4, it is clear that PSO performs better for the two cases.

IV. Conclusion

In the present study, the LLE results for ternary systems of (water + propionic acid or propanol+ 1, 8-cineole) were reported at 291.15 K and 1 atm.

The Othmer–Tobias and Hand correlations were used to check the thermodynamic consistency of the experimental tie lines. In addition, the NRTL model was used to correlate and analyze the experimental data, where good agreement was found between the measured and calculated tie lines with an RMSD less than 0.80%. From the separation factors data, it can be concluded that the separation of propionic acid and propanol from water by extraction was feasible. It is also apparent from Fig. 3 that 1, 8-cineole was an appropriate solvent for the separation of mixtures of water and propionic acid, or propanol.

List of symbols

A	NRTL binary interaction parameters.
a	Othmer–Tobias and Hand equations constant.
b	Othmer–Tobias and Hand equations constant.
x	mass fraction
T	temperature

Superscripts/subscripts

i,j	components
PA	propionic acid
NRTL	non-random, two-liquid
GA	genetic algorithm
PSO	particle swarm optimization
RMSD	Root Mean Squared Deviation

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