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Lactic acid extraction from aqueous solutions with 2-Ethyl-1-hexanol by using experimental liquid-liquid equilibrium data at T=298.2K and atmospheric pressure

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Abstract

Liquid-Liquid equilibrium data for the (water + Lactic acid + 2-ethy-1-hexanol) ternary system were determined at T=298.2K and P=1atm and tie- lines related to the equilibrium data has been shown in the phases diagram. The reliability of the experimental tie-line data for this system was as confirmed using the Hand and the Othmer –Tobias correlations. The tie-line data were correlated by means of the UNIQUAC model for the ternary system. The average root mean square deviation between the observed and calculated mass fractions was 0.66%. The comparison of the extracting capabilities of this solvent by 1-octanol was made with respect to distribution coefficients and separation factors bases. The results show that extraction of lactic acid from aqueous solutions by 2-Ethyl-1-hexanol is possible and 2-Ethyl-1-hexanol is more appropriate than the other octanol isomer.

Keywords: LLE data; Lactic acid; 2-Ethyl-1-hexanol; UNIQUAC model.

Introduction

Recovery and separation of the organic acid from aqueous solutions are of considerable economic importance. Lactic acid is an important carboxylic acid that has large range of industrial and medical application which produced by either microbial fermentation or chemical synthesis [1]. Lactic acid can be used, as a preservative, an antioxidant, and as improver of taste and quality of foods, as a raw material for the production of biodegradable poly lactic acid, as calcium source in calcium lactate at the pharmaceutical industry [2-5]. In bio-production, various fermentation methods have been employed from biomass [6]. However, future purification is required and the extraction of this acid from water is a main problem. Distillation and extraction processes are suitable methods for the purification and separation of water-based products, but distillation is non-applicable in the case of lactic acid because the acid can be deformed at high temperature. Liquid-liquid extraction can be used to separate lactic acid from aqueous solutions; LLE consists of transferring one solute contained in a feed solution to another immiscible liquid (solvent). This method is based on components relative

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solubility in two different immiscible liquids, usually water and an organic solvent. It is an extraction of a substance from one liquid into another liquid phase. The liquid-liquid equilibrium data in the equilibrium conditions (temperature and pressure) between the organic and aqueous phases, physical and chemical properties (such as boiling point, distribution coefficient, separation factor and etc), cost and availability, are very important aspects of the liquid-liquid extraction process [7]. LLE data for the aqueous solution of LA with various organic solvents, mainly alcohols, at various temperatures have been reported in previous publications [8-11]. In the present work, 2-ethyl-1-hexanol (2EH) has been used as an organic solvent for the specification of LLE data for the (water + Lactic Acid+2EH) ternary system. 2EH is a branched and eight-carbon alcohol, which has poor solubility in water, low cost, high boiling point, and can be considered therefore, as good solvent for separation of lactic acid from water. The liquid-liquid equilibrium data for (water+LA+2EH) ternary system at T=298.2K and atmospheric pressure were measured for the first time. Distribution coefficient and separation factor were determined from the tie line data in order to evaluate the extracting ability of the solvent for the separation of LA from water. The results were compared with the other solvents described in past literatures, especially 1-octanol solvent (due to the 2EH and 1-octanol are two Octanol isomers ($C8H18O$)). The liquid-liquid equilibrium data for the (water+LA+2EH) ternary system were predicted by the UNIQUAC (universal quasi chemical) method [12]. UNIQUAC is an activity coefficient model used in description of phase equilibria. At equilibrium, the activites of the component in both phases are equal and the mole fraction X_i^E and X_i^R of the conjugate phases are calculated using the following equation:

$$\gamma_i^E X_i^E = \gamma_i^R X_i^R \qquad (1)$$

where γ_i^E and γ_i^R are the corresponding activity coefficient of component i in extract and raffinate phases. The interaction parameters between each of the main molecules were used to calculate activity coefficients of component i. The values of the UNIQUAC binary interaction parameters for LLE predictions were calculated.

Experimental

Material and procedure

Lactic acid was purchased from Belgian Chemlab with a purity of 85 %. 2-Ethyl-Hexanol was provided by German Merck Company and presented 99 % of purity. Deionized and Distilled water was used in the experiments. The physical properties of the components are presented in Table1.

Table 1. Physical properties of the pure component at T=293.2K and atmospheric pressure

Comp	**n_D**		**$\rho(gr/cm^3)$**	
	exp	**lit**	**exp**	**lit**
Lactic acid	1. 4245	1.4394[13]	1.2020	1.2060[13]
Water	1.3325	1.3330[13]	0.9989	0.9982[13]
2EH	1.4289	1.5290[14]	0.8203	0.8291[14]

The solubility curve (bimodal) was determined by the cloud point method. In a cell glass, homogeneous binary systems (water/ lactic acid and 2EH/ lactic acid) of known mass concentrations were prepared using an analytical balance (Sartorius, CPA3 24S), accurate to 0.0001g, and stirred vigorously using a magnetic stirrer. System temperature was maintained constant at 298.2 ± 0.1 K with a thermostatic bath (Viscotherm VT2, Anton Paar GmbH). The third component was added in the solution using a micropipette 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 by using simple syringes and analyzed in the refractometer (RE 40D, Mettler-Toledo). All the measurements were repeated at least three times. The uncertainty in the mass fraction of the solubility data was estimated to be better than ±0.001. The average of these readings was taken for the component compositions and reported in Table 2. For calibration at T=298.2 K, the equation of variation refractive index with corresponding mass fraction of water($\boldsymbol{w_1}$) was earned as $n_{\mathrm{D}} = -0.1204w_{11} + 1.451$. This equation was presented with coefficient of determination of 0.9958 that has a very good quality.

Tie-lines were measured by preparing mixtures with mass concentration within the diagram region delimited by the solubility curve to ensure phase split. Ternary mixtures were agitated vigorously with a magnetic stirrer for 4 hours in an equilibrium glass cell. Then, the system rested for a period of 6 hours, allowing the completeness of the phase split, regarded by a clean and well defined phase boundary between the phases. The aqueous and organic phase’s samples were weighed and analyzed to determine the LLE tie lines. The refractive indices of samples were measured by refractometer. The concentrations of lactic acid in organic and aqueous phases were determined by potentiometric NaOH titration in the presence of phenolphthalein indicator. Karl-fischer (870 KF Titrino plus) method [15] was used to calculate the water content of the organic phase samples. The water mass fraction of the aqueous phase samples was determined from the calibration equation.

Table 2. Experimental solubility curve data for (water + lactic acid+2EH) at T=298.2 K[a]

w_1 (water)	w_2 (lactic acid)	w_3 (2EH)
0.0226	0.0884	0.8890
0.0253	0.1717	0.8030
0.0288	0.2450	0.7262
0.0474	0.3647	0.5879
0.0642	0.4625	0.4733
0.0861	0.5578	0.3561
0.1125	0.6411	0.2464
0.1492	0.7045	0.1463
0.1955	0.7291	0.0754
0.2652	0.6998	0.0350
0.3017	0.6777	0.0206
0.4201	0.5677	0.0122
0.5240	0.4698	0.0062
0.6112	0.3844	0.0044
0.6893	0.3086	0.0021
0.7608	0.2377	0.0015
0.8323	0.1668	0.0009
0.8914	0.1081	0.0005
0.9557	0.0440	0.0003

[a]Standard uncertainties u are u(T)=0.1 K and u(w) = 0.001

Results and discussion

The experimental tie-line data for the ternary system of (water + lactic acid + 2-ethyle-1-hexanol) were determined at T = 298.2 K and atmospheric pressure. The experimental tie-line composition of the equilibrium phases for this ternary system is listed in Table 3. Also, the LLE diagram for this ternary system is plotted and shown in Figure 1. Since (lactic acid + water) and (2-ethyl-1-hexanol + lactic acid) are two liquid pairs that are completely miscible and the only liquid pair (water + 2-ethyl-1-hexanol) is partially miscible, the ternary system behaves as a type -1 LLE[16]. The slope of tie- lines in Figure 1 indicates that lactic acid is more soluble in water than in 2- ethyl-1-hexanol. In order to verify the consistency of experimentally tie line data presented in this work, mass fraction in both phases were related by the Othmer-Tobias (eq.2) [17]and Hand (eq.3) [18] tests.

$$ln\ \frac{1-w_{33}}{w_{33}} = A + B\ ln\left(\frac{1-w_{11}}{w_{11}}\right) \qquad (2)$$

$$\ln \frac{w_{21}}{w_{11}} = C + D \ln \frac{w_{23}}{w_{33}} \qquad (3)$$

Where w_{11}, w_{21} is mass fraction of water and the acid in the aqueous-rich phase, w_{23} and w_{33} are mass fractions of the acid and the solvent in the organic rich phase. A,B,C and D are the parameters of the Othmer–Tobias and the Hand correlations, respectively. The parameters of the Othmer–Tobias and Hand correlations, for this ternary system, are listed in Table 4. The Othmer–Tobias and the Hand plots for the system at T=298.2K are showed in Figure 2. The correlation factor (R^2), and the linearity of the plots indicates the degree of reliability of the related data. Distribution coefficient of acid and water (D_2,D_1) respectively, and separation factor (S) are appropriate criterias to indicate the ability of organic solvent in the extraction of solute. Equations 4, 5 and 6 are used to calculate these factors,

$$D_1 = w_{13}/w_{11} \qquad (4)$$

$$D_2 = w_{23}/w_{21} \qquad (5)$$

$$S = D_2/D_1 \qquad (6)$$

Where w_{13}, w_{23} mass fraction of water and lactic acid in solvent-rich is phase, and w_{11},w_{21} is mass fraction of water and lactic acid in water-rich is phase. The distribution coefficients and separation factors are given in Table 5. Since the 2EH and 1-Octanol are Octanol isomers, the variation of experimental distribution coefficients lactic acid and separation factor as a function of the mass fraction of the solute (LA) in aqueous phase for the studied ternary system at T=298.2K were compared with 1-octanol (that investigated by Shahin *et al.* [10]) in Figure 3. As can be seen, the value of separation factor for 2-ethyl-1-hexanol is more than the 1-Octanol at T=298.2K. However, the branched primary alcohol, 2EH, has the advantage of higher separation factor. Also**,** the experimental separation factor (the highest value) earned in this work, were compared with other organic solvents reported in previous publications (Figure 4).

Table 3. Experimental tie line data in mass fraction for (Water+LA+2EH) at T=298.2K and p=1atm[a]

Aqueous phase mass fraction				Organic phase mass fraction			
w_1(water)		w_2(LA)		w_1(water)		w_2(LA)	
Exp	**UNIQUAC**	**Exp**	**UNIQUAC**	**Exp**	**UNIQUAC**	**Exp**	**UNIQUAC**
0.8572	0.8519	0.1410	0.1463	0.0210	0.0220	0.0345	0.0355
0.7612	0.7667	0.2365	0.2309	0.0228	0.0231	0.0582	0.0576
0.6818	0.7000	0.3154	0.2968	0.0237	0.0241	0.0779	0.0763
0.6318	0.6387	0.3644	0.3574	0.0260	0.0251	0.0976	0.0955
0.5757	0.5765	0.4192	0.4184	0.0269	0.0262	0.1168	0.1175
0.5408	0.5234	0.4523	0.4702	0.0280	0.0273	0.1343	0.1392

[a] Standard uncertainties u are u(T)=0.1 K and u(w) = 0.001

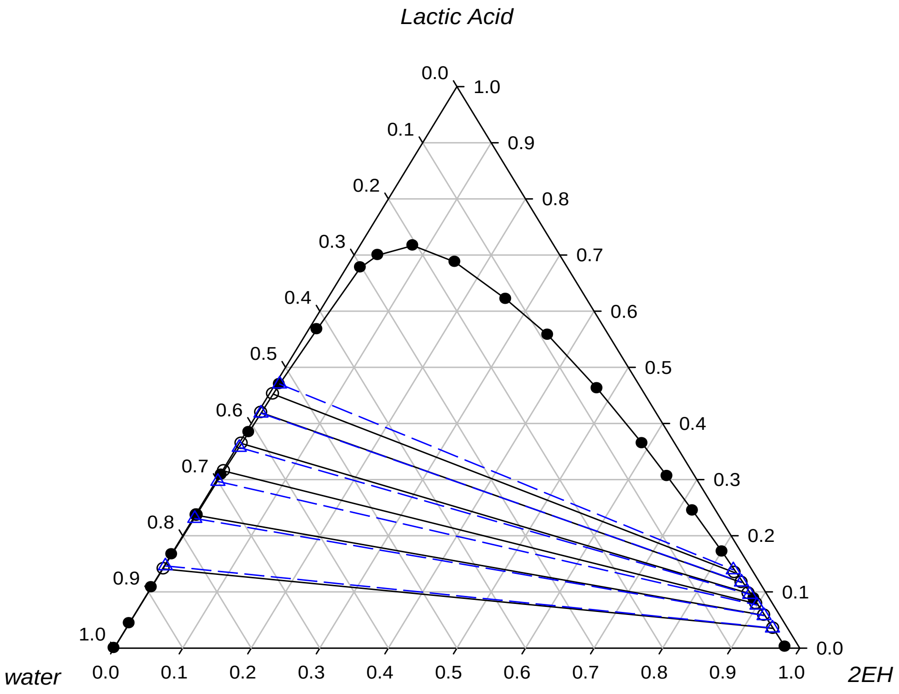

Figure 1. Phase diagram for the ternary systems at T = 298.2 K;(●) solubility data points, (○) experimental points, (△) UNIQUAC calculated points

Table 4. Othmer-Tobias and Hand equations constants and the correlation factor

Othmer –Tobias			**Hand**		
A	**B**	**R^2**	**C**	**D**	**R^2**
-1.568	0.725	0.993	1.888	1.109	0.997

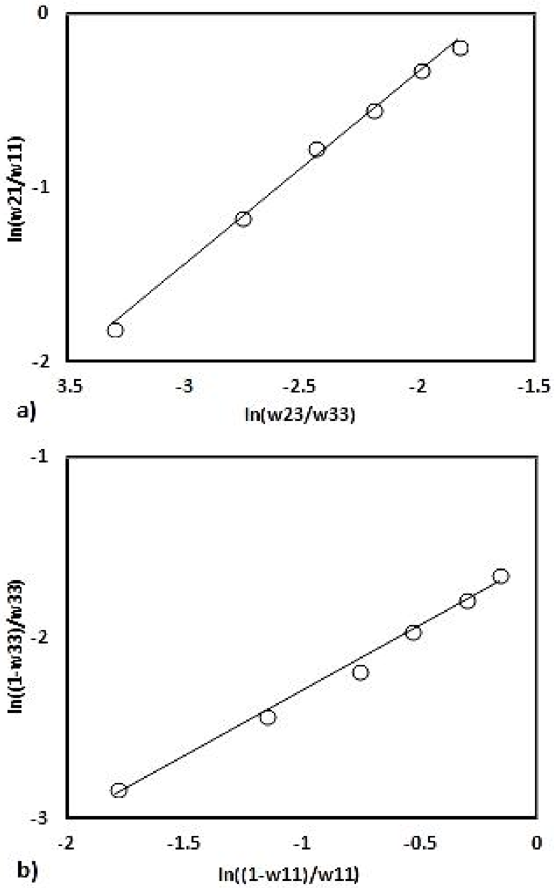

Figure 2. Quality tests for water (1), lactic acid (2) and 2EH (3): (a) Hand correlation; (b) Othmer-Tobia correlation

Table 5. Distribution coefficients for water (D_1) and lactic acid (D_2), and separation factors (S)

D_1	D_2	S
0.024	0.24	10
0.030	0.25	8.33
0.035	0.25	7.14
0.041	0.27	6.59
0.047	0.28	5.96
0.052	0.30	5.77

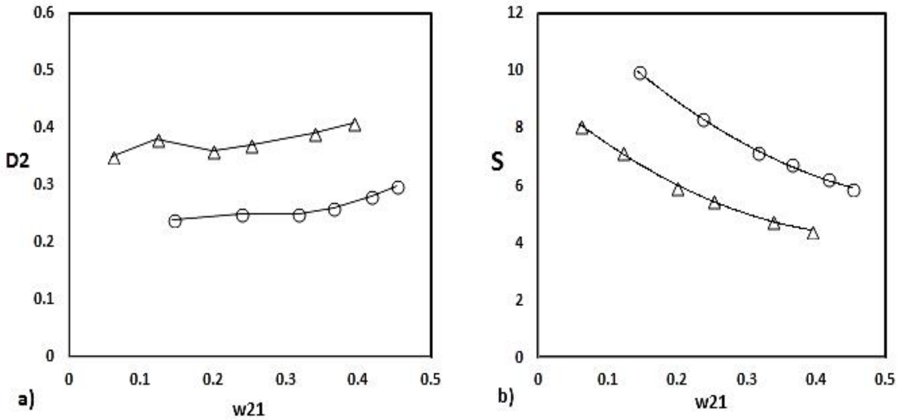

Figure 3. Distribution coefficients (a) and separation factors (b) plotted against the mass fraction of lactic acid in the aqueous phase,w_{21} , at T=298.15K for ternary system (water + lactic acid +(○) 2-Ethyle-1-hexanol[this work],and(△)1-octanol[10]

Correlated data for the tie lines in terms of concentrations of each compound in the two phases in equilibrium were adjusted using the UNIQUAC model [12]. The UNIQUAC structural parameters (*r* and *q*) were taken from Refs [19,20] and listed in Table 6. The correlated data for the ternary system at T=298.2K is given in Table 3. Figure 3 shows a comparison between the generated and experimental tie-line data. The LLE data were used to determine the UNIQUAC (a_{ij}) binary interaction parameters that may be written as

$$a_{ij} = \frac{u_{ij}-u_{jj}}{R} \qquad (7)$$

a_{ij} is expressed in K and represents the energy interactions between an *i-j* pair of molecules.

The parameter u_{ij} characterize the UNIQUAC interaction energy. This UNIQUAC interaction parameter can be correlated with the term τ_{ij}. The adjustable parameter (τ_{ij}) in the UNIQUAC equation may be expressed as

$$\tau_{ij} = \left(-\frac{\Delta u_{ij}}{RT}\right) = \exp\left(-\frac{a_{ij}}{T}\right) \qquad (8)$$

The objective function developed by sorensen [21] was used to optimize the equilibrium model. The objective function is sum of the squares of the difference between the experimental and calculated mass fractions. The root-mean square deviation (*rmsd*) values were used to distinguish final optimization results.The root-mean square deviation (*rmsd*) between the experimental and calculated compositions were determined according to the following equation:

$$RMSD\% = 100\sqrt{\frac{\sum_{k=1}^{n}\sum_{j=1}^{2}\sum_{i=1}^{3}(w_{ijk}^{exp}-w_{ijk}^{cal})^2}{6n}} \qquad (9)$$

where n is the number of tie-lines, w^{exp} indicates the experimental and, w^{cal} is the calculated mass fraction, i indexes components and j indexes phases. The UNIQUAC binary interaction parameters for the investigated systems are shown in Table 7.

Table 6. The UNIQUAC structure parameters for pure component

component	r	q
Lactic acid	3.65	3.50
water	0.92	1.40
2EH	6.20	5.10

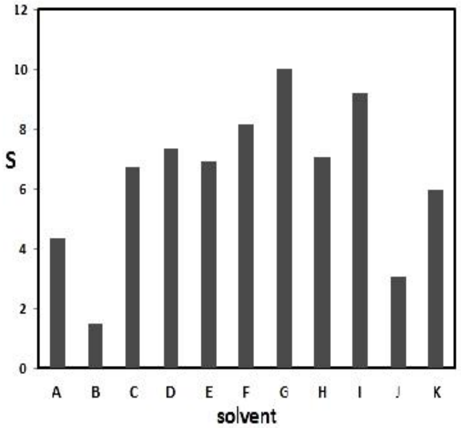

Figure 4. separation factor (the highest value) for the (water+LA+ alcoholic solvents) ternary system at T=298.K,P=1 atm ,taken from previous publication [8-11], (A)1-boutanol, (B)2-boutanol, (C)1-pentanol, (D)1-hexanol (E)1-heptanol, (F)octanol, (G)2EH{this work}, (H)nonanol (I)decanol, (J)IMBK, (K)butylacetate

Table 7. UNIQUAC binary interaction parameter and rmsd value for the ternary system

Pair	a_{ij}	a_{ji}	*rmsd*
1-2	101.13	-4.93	
2-3	-382.37	205.68	0.66
1-3	-194.09	-349.332	

Conclusion

Solubility and tie-line data for the (water + Lactic acid + 2-ethyl-1-hexanol) ternary system were determined at T = 298.2 K. The ternary system exposed type-1 behaviour of LLE. The Othmer-Tobias and Hand equations were verified for consistency of tie line data. UNIQUAC model was used to correlate the experimental LLE data. The average *rmsd* value between the observed and calculated mass fractions with a reasonable error was 0.66%. The separation factor and distribution coefficient were calculated for the organic solvent (2EH) used in this work and were compared with Octanol isomer other (1-Octanol) and organic solvent. Experimental results indicate that extraction of lactic acid by 2-ethyl-1-hexanol is possible. Branching on the solvent molecule can improve the separation factor. Generally, alcoholic solvents (such as 2EH) by having high polar hydroxyl group in their structural molecule have been adequately able to separate lactic acid from water.

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