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Liquid−Liquid Equilibria of Water + 1-Butanol + 2-Ethyl-1-hexanol System

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Liquid−liquid equilibria (LLE) for the ternary system water + 1-butanol + 2-ethyl-1-hexanol at (298.2, 303.2, 308.2, and 313.2) K are reported. A type-2 liquid−liquid phase diagram was obtained for this ternary system. The UNIQUAC model was used to correlate the LLE data with a root-mean-square deviation value of 1.08%. The UNIQUAC interaction parameters between each pair of components in the system were obtained using the experimental results. The effect of 1-butanol addition on mutual solubility of 2-ethyl-1-hexanol and water was also investigated at different temperatures.

1. Introduction

The importance of the availability of liquid−liquid equilibrium data (LLE) in the design of many chemical processes and separation operations have been the subject of much interest in recent years. Many researchers have investigated multicomponent systems in order to understand and provide further information about the phase behavior and the thermodynamic properties of such systems.[1−8] We have recently reported[9,10] LLE data for ternary mixtures of water + *tert*-butyl alcohol + 2-ethyl-1-hexanol and water + ethanol + 2-ethyl-1-hexanol at different temperatures, where a type-1 liquid−liquid phase diagram was obtained for the ternary systems. In both systems, the correlated results were in good agreement with the observed results. As a continuation of that previous work, we present the LLE data for the ternary system water + 1-butanol + 2-ethyl-1-hexanol at (298.2, 303.2, 308.2, and 313.2) K. The experimental results were correlated using the UNIQUAC model.[11,12] Recently, Gremer et al.[13] have reported vapor−liquid equilibria and vapor−liquid−liquid equilibria measurements of the same system (i.e., water, 1-butanol, and 2-ethyl-1-hexanol) in the temperature range of 373−473 K, and their investigation may be important and provide useful information about the phase behavior and mutual solubility of the water−2-ethyl-1-hexanol and water−1-butanol mixtures.

This work presents useful LLE data for the extraction of 1-butanol from aqueous solution. The separation of alcohols from aqueous solutions using the liquid−liquid extraction technique is industrially and scientifically important.[14] To minimize design cost and optimize extraction, many organic solvents have been investigated for the extraction of dilute alcohols such as 1-butanol from aqueous mixtures. Roddy[15] has measured and reported the distribution coefficients and separation factors for ethanol and water in several organic solvents. According to his reports, alcohols with a high polar −OH group located on a primary carbon are very good extractants for ethanol. He concluded that branching on the alcohol solvent molecules improve the distribution coefficient.

In the present work, 2-ethyl-1-hexanol is used as an organic solvent, which has suitable molecular structure, low cost, a high boiling point, and very low solubility in water, and is, therefore, a good solvent with a high ability for extraction of 1-butanol from aqueous solution.[16,17] The effect of 1-butanol addition on solubility of water in 2-ethyl-1-hexanol (organic phase) was also investigated at (298.2, 303.2, 308.2, and 313.2) K.

2. Experimental Section

2-Ethyl-1-hexanol and 1-butanol were obtained from Merck with purities of 99.5% and 99.8%, respectively. The purity of these materials was checked by gas chromatography and used without further purification. Distilled water was used throughout all experiments.

The equilibrium data were determined using the experimental apparatus of a 300-mL glass cell, where the temperature of the cell was controlled by a water jacket and maintained with an uncertainly of within ±0.1 K. A magnetic stirrer provided sufficient agitation within the apparatus. The prepared mixtures were introduced into the extraction cell, were stirred for 2 h, and were then left to settle for 4 h for phase separation. Samples of less than 1 μL were carefully taken by a syringe from the upper layer through a sampling tap from the lower layer. Both phases were analyzed using a Konik gas chromatography (GC) equipped with a thermal conductivity detector (TCD) and Shimadzu C-R2AX integrator. A 2 m × 2 mm column packed with 10% porapak QS 80/100 was used to separate the components. The injection temperature was 523.2 K, and the detector temperature was 549.2 K. The carrier gas (helium) flow rate was maintained at 46 mL/min.

The TCD's response was calibrated with 2-ethyl-1-hexanol as an internal standard. The calibration samples were prepared by weighing with an analytical balance accurate to within ±0.0001 g. The calibration equations were used to convert the area fraction into mol fraction. Calibration coefficients were obtained by fitting a straight line to the calibration results for each composition range. All measurements are performed in triplicate. The estimated uncertainties in the mol fraction were about 0.0005.

3. Results and Discussion

3.1. LLE Measurements. The LLE measurements for the ternary system of water + 1-butanol + 2-ethyl-1-

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Table 1. Experimental and Calculated LLE for the Ternary System Water (1) + 1-Butanol (2) + 2-Ethyl-1-hexanol (3) at (298.2, 303.2, 308.2, and 313.2) K

aqueous-phase mol fraction				organic-phase mol fraction			
x_1 (water)		x_2 (1-butanol)		x_1 (water)		x_2 (1-butanol)	
exp	UNIQUAC	exp	UNIQUAC	exp	UNIQUAC	exp	UNIQUAC
				298.2 K			
0.9948	0.9947	0.0047	0.0051	0.1351	0.1270	0.0990	0.1200
0.9921	0.9901	0.0072	0.0093	0.1610	0.1588	0.2292	0.2370
0.9907	0.9895	0.0086	0.0100	0.1909	0.1960	0.3019	0.3411
0.9869	0.9892	0.0124	0.0105	0.2240	0.2341	0.3740	0.4110
0.9832	0.9890	0.0159	0.0102	0.2660	0.2715	0.4401	0.4631
0.9816	0.9881	0.0175	0.0113	0.3161	0.3180	0.5080	0.5293
0.9807	0.9861	0.0181	0.0131	0.4101	0.4121	0.5896	0.5879
				303.2 K			
0.9959	0.9980	0.0039	0.0015	0.1430	0.1490	0.1547	0.1843
0.9908	0.9940	0.0066	0.0055	0.1644	0.1760	0.2746	0.2616
0.9896	0.9910	0.0011	0.0082	0.1930	0.2040	0.3437	0.3301
0.9885	0.9920	0.0086	0.0079	0.2724	0.2661	0.4566	0.4510
0.9828	0.9870	0.0144	0.0125	0.2841	0.2920	0.4869	0.4965
0.9814	0.9850	0.0161	0.0148	0.3233	0.3311	0.5011	0.5540
0.9744	0.9830	0.0175	0.0150	0.4011	0.4039	0.5989	0.5961
				308.2 K			
0.9959	0.9980	0.0036	0.0015	0.1569	0.1510	0.1221	0.1278
0.9944	0.9970	0.0050	0.0024	0.1864	0.1790	0.3167	0.3251
0.9928	0.9927	0.0061	0.0062	0.2314	0.2330	0.3933	0.3921
0.9925	0.9911	0.0071	0.0085	0.2544	0.2650	0.4188	0.3949
0.9831	0.9863	0.0161	0.0130	0.2784	0.2730	0.4795	0.4680
0.9820	0.9840	0.0171	0.0152	0.3043	0.2971	0.5042	0.4660
0.9808	0.9809	0.0189	0.0182	0.3507	0.3040	0.5354	0.6141
				313.2 K			
0.9960	0.9983	0.0038	0.0015	0.1434	0.1520	0.1202	0.1161
0.9924	0.9964	0.0072	0.0032	0.1664	0.1730	0.2395	0.2000
0.9898	0.9929	0.0096	0.0062	0.1950	0.2000	0.3133	0.3110
0.9851	0.9900	0.0140	0.0096	0.2300	0.2360	0.3903	0.3770
0.9817	0.9842	0.0172	0.0129	0.2674	0.2820	0.4607	0.4400
0.9836	0.9835	0.0154	0.0152	0.3188	0.3219	0.5427	0.5130
0.9813	0.9804	0.0175	0.0182	0.4073	0.4150	0.5927	0.5850

hexanol were made at atmospheric pressure in the temperature range of (298.2 to 313.2) K. The experimental LLE data for this ternary system are reported in Table 1. The experimental data together with calculated tie lines for this ternary system at a temperature of 298.2 K were plotted and shown in Figure 1. Since 2-ethyl-1-hexanol + 1-butanol is the only liquid pair that is completely miscible and the two liquid pairs (water + 1-butanol) and (water + 2-ethyl-1-hexanol) are partially miscible, the ternary system behaves as a type-2 LLE. As expected for a type-2 system, the phase diagram shows no plait point. It is found that water dissolved noticeably in the organic phase, while only slight amounts of 2-ethyl-1-hexanol were detected in the aqueous phase. The area of the two-phase region depends on the solubility of water in the organic phase.

Since the measured LLE data in the present work can be used for the extraction of 1-butanol from aqueous solution, the very low solubility of 2-ethyl-1-hexanol in water and the effect of its addition on the organic-phase composition seems to be important. As it can be seen from Table 1, the value of $x_{1-\text{butanol}}/x_{\text{water}}$ first increases with 2-ethyl-1-hexanol addition, but then it decreases at high

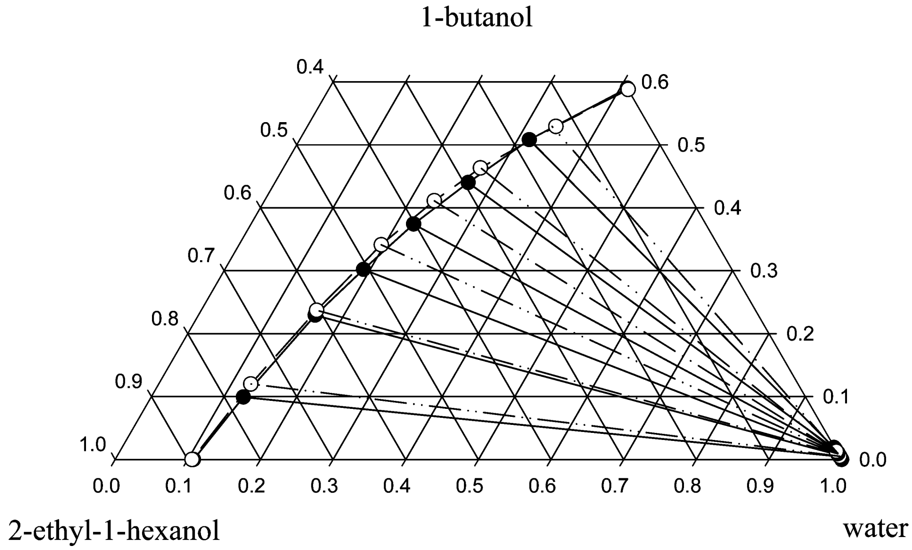

Figure 1. Experimental (●) and correlated UNIQUAC (○) LLE data at 298.2 K.

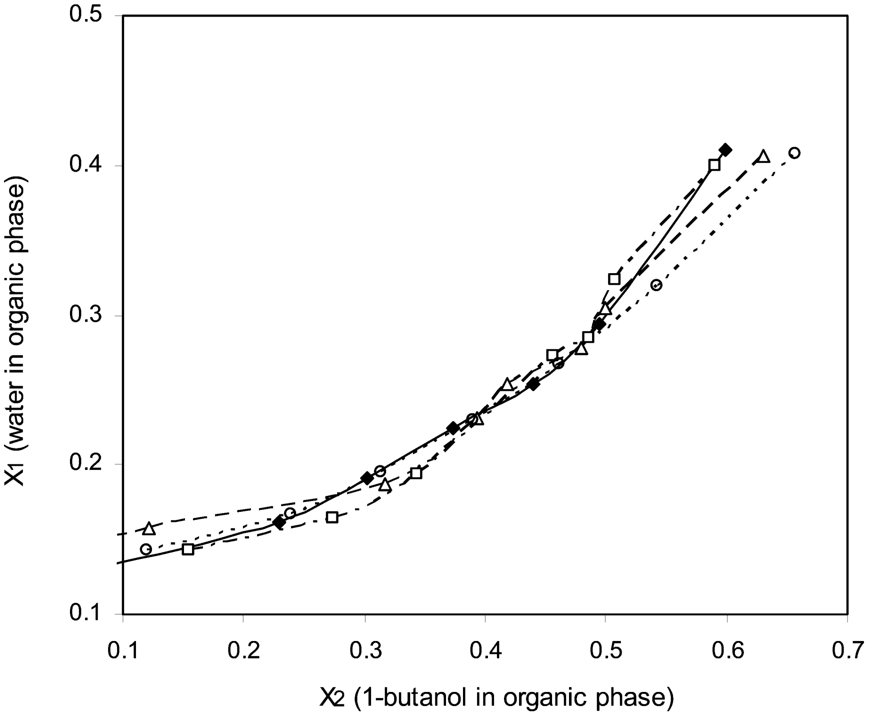

Figure 2. Effects of 1-butanol addition on solubility of water in 2-ethyl-1-hexanol (organic phase) for water (1) + 1-butanol (2) + 2-ethyl-1-hexanol (3) system at different temperatures: ◆, 298.2 K; □, 303.2 K; △, 308.2 K; ○, 313.2 K.

solvent compositions at 298.2 K. Similar results were obtained for the other temperatures.

The effect of *n*-butyl alcohol addition on the solubility of water in 2-ethyl-1-hexanol (organic phase) was also investigated at different temperatures (298.2, 303.2, 308.2, and 313.2 K). Figure 2 shows that the solubility of water in 2-ethyl-1-hexanol increases with amounts of 1-butanol added to the water + 2-ethyl-hexanol mixture. The temperature in the range of the study has only a small effect on the solubility of water in 2-ethyl-1-hexanol. Similar behavior was obtained and reported on the addition of *tert*-butyl alcohol and ethanol on the solubility of water in 2-ethyl-1-hexanol.[9,10] In both systems, the temperature has no noticeable effect on solubility of water in the organic phase.

3.2. LLE Calculation. The experimental LLE data of a ternary system can be correlated using the UNIQUAC model. The interaction parameters between each pair of components in the system are used to estimate the activity coefficients. The mole fractions x_i^{E} and x_i^{R} of LLE phases (extracted phase and raffinate phase) can be determined using the following equations

$$(\gamma_i x_i)^{\mathrm{E}} = (\gamma_i x_i)^{\mathrm{R}} \tag{1}$$

$$\sum x_i^{\mathrm{E}} = \sum x_i^{\mathrm{R}} = 1 \tag{2}$$

Here γ_i^{E} and γ_i^{R} are the corresponding activity coefficients of component *i* in the extracted (solvent) phase and the raffinate (aqueous) phase. The UNIQUAC equation for the liquid-phase activity coefficient is represented as follows[12]

$$\ln \gamma_i = \ln \gamma_i \text{ (combinatorial)} + \ln \gamma_i \text{ (residual)} \tag{3}$$

The combinatorial and residual parts of the activity coefficient are due to the difference in shape and energy of the molecules, recpectively. The combinational and residual parts of the activity coefficient can be written as follows

Table 2. The UNIQUAC Structural Parameters

components	*r*	*q*
1-butanol	3.45	3.05
2-ethyl-1-hexanol	6.15	5.02
water	0.92	1.40

$$\ln \gamma_i^{c} = \ln\left(\frac{\Phi_i}{x_i}\right) + \frac{z}{2} q_i \ln\left(\frac{\theta_i}{\Phi_i}\right) + \iota_{\iota} - \frac{\phi_i}{x_i}\sum_{j=1}^{c} x_j \iota_j \tag{4}$$

$$\ln \gamma_i^{\mathrm{R}} = q_i\left[1 - \ln\left(\sum_{j=1}^{c} \theta_j \tau_{ji}\right) - \sum_{j=1}^{c}\left(\frac{\theta_j \tau_{ij}}{\sum_{k=1}^{c} \theta_k \tau_{kj}}\right)\right] \tag{5}$$

Here τ_{ij} is an adjustable parameter in the UNIQUAC equation. The parameter Φ_i (segment fraction) and θ_i (area fraction) are given by the following equations

$$\Phi_i = \frac{x_i r_i}{\sum_{i=1}^{c} x_i r_i} \qquad \theta_i = \frac{x_i q_i}{\sum_{i=1}^{c} x_i q_i} \tag{6}$$

The UNIQUAC structural parameters *r* and *q* were calculated from group contribution data that has been previously reported.[12] The values of *r* and *q* used in the UNIQUAC equation are presented in Table 2. The objective function developed by Sørensen[18] was used to optimize the equilibrium model. The objective function is the sum of the squares of the difference between the experimental and calculated mol fractions.

The correlate results together with the experimental data are reported in Table 1. Figure 1 compares the observed and calculated LLE data for the ternary system of water + 1-butanol + 2-ethyl-1-hexanol at a temperature

Table 3. RMSD % Values in the Correlation by UNIQUAC, at Each Temperature, for the Ternary System Water (1) + 1-Butanol (2) + 2-Ethyl-1-hexanol (3)

	aqueous phase		organic phase		
T/K	x_1 (water)	x_2 (1-butanol)	x_1 (water)	x_2 (1-butanol)	avg
298.2	0.41	0.35	0.58	2.51	0.97
303.2	0.44	0.31	0.81	2.44	1.00
308.2	0.20	0.21	1.88	3.48	1.44
313.2	0.30	0.32	0.81	2.11	0.89
RMSD%					1.08

Table 4. Optimized UNIQUAC Binary Interaction Parameter a_{ij} (K) for the System Water (1) + 1-Butanol (2) + 2-Ethyl-1-hexanol (3) at Different Temperatures

	298.2 K	303.2 K	308.2 K	313.2 K
a_{12}	192.600	189.06	187.32	184.87
a_{21}	83.12	90.40	102.48	96.50
a_{13}	211.46	209.40	207.88	206.50
a_{31}	209.65	217.89	223.10	225.81
a_{23}	−32.100	−32.65	−33.09	−33.31
a_{32}	47.23	47.97	48.85	48.96

Table 5. Optimized UNIQUAC Binary Interaction Parameter a_{ij} (K) with Dependence of Temperature (T in K)

a_{ij}/K	a_{ji}/K
$a_{12} = 340.86 - 0.499T$	$a_{21} = -226.10 + 1.044T$
$a_{13} = 309.06 - 0.328T$	$a_{31} = -109.09 + 1.0738T$
$a_{23} = -7.9076 - 0.0814T$	$a_{32} = 13.023 + 0.115T$

of 298.2 K. The calculated tie lines (dashed lines) in Figure 1 were obtained using the UNIQUAC equation and are in relatively good agreement with the experimental data (solid lines).

The root-mean-square deviation (RMSD) value was calculated from the difference between the experimental and calculated mol fractions according to the following equation

$$\text{RMSD \%} = 100\left(\sum_{k}^{n}\left[\frac{\sum_{i}^{3}\sum_{j}^{2}(x_{\text{i}},\text{exp} - x_{\text{i}},\text{calc})_j^{2}}{6n}\right]\right)^{1/2} \tag{7}$$

where n is the number of tie lines, x_{exp} and x_{calc} indicate the experimental and calculated mol fractions, and the subscript i represents index components, j represents phases, and $k = 1, 2, ..., n$. The average (RMSD %) between the observed and calculated mole fractions was 1.08% as reported in Table 3.

The UNIQUAC interaction parameters can be correlated with temperature with the term τ_{ij}

$$\tau_{ij} = \exp(-a_{ij}/T) \tag{8}$$

where a_{ij} is expressed in K, is the UNIQUAC parameter with temperature independence, and represents the energy interactions between an $i-j$ pair of molecules. The values of the interaction parameter (a_{ij} and a_{ji}) between water, 1-butanol, and 2-ethyl-1-hexanol were determined using the observed LLE data at different temperatures are shown in Table 4. It can be seen that there is a linear increase in the interaction parameters with an increase in temperature. Table 5 shows the values obtained for the interaction parameters assuming that there is a linear relation with temperature.

4. Conclusions

Tie-line data of the ternary system consisting of water + 1-butanol + 2-ethyl-1-hexanol were obtained at (298.2, 303.2, 308.2, and 313.2) K. In comparison with the type-1 ternary systems water + ethanol + 2-ethyl-1-hexanol and water + *tert*-butyl alcohol + 2-ethyl-1-hexanol, which have been reported in our previous papers,[9,10] this system exhibited a type-2 behavior of LLE. The solubility of water in 2-ethyl-1-hexanol increases with amounts of 1-butanol added to the water + 2-ethyl-hexanol mixture.

The UNIQUAC model was used to correlate and analyze the experimental data at (298.2, 303.2, 308.2, and 313.2) K with an RMSD value of 1.08%, where the RMSD value is a measure of the precision of the correlation. In general, the LLE data of this ternary system can be correlated fairly well with this equilibrium model.

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