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Experimental and Theoretical Study of the Phase Equilibria in Ternary Aqueous Mixtures of 1,4-Butanediol with Alcohols at 298.2 K

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Ternary liquid−liquid equilibrium (LLE) data for the mixtures of water + 1,4-butanediol + organic solvent (cyclohexanol, 2-ethyl-1-hexanol, and 1-decanol) were determined at 298.2 K and atmospheric pressure. These three ternary systems exhibit type-1 behavior of LLE. The immiscibility region was found to be larger for the branched aliphatic alcohol, 2-ethyl-1-hexanol. The experimental ternary LLE data were correlated using the UNIQUAC and NRTL models, and the binary interaction parameters were obtained. The reliability of the experimental tie-line data was tested through the Othmer−Tobias and Bachman correlation equations. Distribution coefficients and separation factors were calculated to evaluate the extracting capability of the solvents. The LLE results show that 2-ethyl-1-hexanol may be considered to be a reliable organic solvent for the extraction of 1,4-butanediol from aqueous solutions.

Introduction

Liquid-phase equilibrium data of aqueous mixtures with organic solvents play an important role in the design and development of separation processes. In particular, liquid−liquid equilibria (LLE) investigations for ternary mixtures are important in the evaluation of industrial units for solvent extraction processes. The accurate interpretation of phase equilibria and thermodynamic behavior for the different ternary mixtures is a fundamental and important key to improving solvent extraction techniques.[1−11] As in many separation processes, the type of solvent and temperature, which influence the equilibrium characteristics of the solute extraction from aqueous solutions, play an essential role in the effectiveness of the separation.[12−15]

1,4-Butanediol is a clear viscous liquid that melts at 293.2 K. It is a widely used bifunctional alcohol, that has many industrial and medical applications.[16,17] 1,4-Butanediol is used industrially as an organic solvent and as an intermediate in manufacturing some types of plastics and synthetic fibers. It is extensively used as additives in the textile industry. Despite the industrial importance of 1,4-butanediol, on the basis of the authors' literature review, relatively few investigations on the thermodynamic properties and phase behavior of 1,4-butanediol and its aqueous mixture have been reported in the literature.[18−21]

Because a detailed evaluation of solvents for the extraction of 1,4-butanediol is not available in the literature, in this study, heavy alcohols (cyclohexanol, 2-ethyl-1-hexanol, and 1-decanol) were chosen as organic solvents for recovering 1,4-butanediol from water. These solvents have already been used as extractants to determine LLE data for many ternary mixtures.[22−26] From practical and economical aspects, an efficient solvent should have a suitable molecular structure, low cost, low toxicity, high boiling temperature, different density from water, low solubility in water, large distribution coefficient, and high separation factor. The heavy alcohols used in this research as organic solvents have many of these properties.

The aim of this study is to present the phase behavior and LLE data for the three ternary systems (water + 1,4-butanediol + cyclohexane), (water + 1,4-butanediol + 2-ethyl-1-hexanol), and (water + 1,4-butanediol + 1-decanol) at $T = 298.2$ K and atmospheric pressure. Phase diagrams were also obtained by solubility and tie-line data.

Distribution coefficients and separation factors were determined from the tie-line data to establish the extracting capability of the solvents and the possibility of the use of these solvents for the separation of (water + 1,4-butanediol) mixtures. The experimental data were correlated using the UNIQUAC[27] and NRTL[28] equations, and the values for the interaction parameter were obtained and compared. In general, according to these comparisons, the UNIQUAC and NRTL models are applicable for the LLE calculations of the investigated systems.

Experimental Section

Materials. All chemicals used in this work (mass fraction purity > 99 %) were obtained from Merck. The chemicals were used without further purification. Deionized and redistilled water was used throughout all experiments.

Apparatus and Procedure. The solubility curves for the ternary mixtures were determined by the cloud point method in an equilibrium glass cell. The prepared binary mixtures of known compositions were introduced to the glass cell. The temperature of the cell was controlled by a water jacket and maintained with an accuracy of within ± 0.1 K. The third component was progressively added using a microburet. The end point was determined by observing the transition from a homogeneous to a heterogeneous mixture. All mixtures were prepared by weighing with an analytical balance accurate to within ± 0.0001 g.

A 250 mL glass cell connected to a thermostat was made to measure the LLE data. We determined the equilibrium data by preparing the ternary mixtures of known compositions. A water jacket was used to control the temperature of the cell to within ± 0.1 K. The prepared mixtures were placed in the extraction

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Table 1. Experimental, UNIQUAC Correlated, and NRTL (α = 0.2) Correlated Tie-Line Data in the Aqueous and Organic Phases for (Water (1) + 1,4-Butanediol (2) + Solvent (3)) at 298.2 K

aqueous phase						organic phase					
x_1 (water)			x_2 (1,4-butanediol)			x_1 (water)			x_2 (1,4-butanediol)		
exptl	UNIQ.	NRTL	exptl	UNIQ.	NRTL	exptl	UNIQ.	NRTL	exptl	UNIQ.	NRTL
Water + 1,4-Butanediol + 2-Ethyl-1-hexanol											
0.9284	0.9187	0.9298	0.0681	0.0777	0.0664	0.0229	0.0209	0.0233	0.0390	0.0318	0.0390
0.8641	0.8553	0.8730	0.1296	0.1390	0.1209	0.0237	0.0236	0.0237	0.0509	0.0504	0.0510
0.7611	0.7557	0.7402	0.2279	0.2342	0.2450	0.0239	0.0259	0.0242	0.0519	0.0663	0.0520
0.7300	0.7263	0.7096	0.2574	0.2618	0.2788	0.0245	0.0263	0.0246	0.0596	0.0695	0.0589
0.5111	0.5370	0.5448	0.4640	0.4344	0.4274	0.0287	0.0280	0.0280	0.1101	0.0828	0.1080
Water + 1,4-Butanediol + 1-Decanol											
0.8290	0.8247	0.8219	0.1653	0.1697	0.1726	0.0136	0.0185	0.0186	0.0155	0.0151	0.0156
0.7345	0.7232	0.7280	0.2525	0.2642	0.2592	0.0192	0.0205	0.0204	0.0267	0.0258	0.0260
0.6343	0.6263	0.6362	0.3432	0.3470	0.3362	0.0245	0.0228	0.0225	0.0365	0.0375	0.0375
0.5245	0.5494	0.5610	0.4311	0.4030	0.3903	0.0274	0.0238	0.0234	0.0418	0.0423	0.0422
0.4650	0.4847	0.4960	0.4640	0.4403	0.4270	0.0415	0.0298	0.0260	0.0670	0.0690	0.0703
Water + 1,4-Butanediol + Cyclohexanol											
0.8048	0.8045	0.8048	0.1346	0.1355	0.1347	0.1472	0.1637	0.1517	0.0419	0.0440	0.0427
0.7042	0.7102	0.7063	0.2075	0.2051	0.2074	0.1765	0.1818	0.1765	0.0882	0.0936	0.0901
0.6026	0.6035	0.6015	0.2679	0.2700	0.2719	0.2223	0.2182	0.2201	0.1685	0.1731	0.1709
0.5933	0.5929	0.5910	0.2750	0.2750	0.2773	0.2301	0.2230	0.2254	0.1806	0.1812	0.1797
0.5374	0.5476	0.5440	0.3103	0.3011	0.3000	0.2521	0.2474	0.2513	0.2180	0.2171	0.2182

cell and were vigorously agitated by a magnetic stirrer for 4 h. The mixtures were then settled for 4 h at constant system temperature to separate completely into two liquid phases. After separation, samples of both phases were transparent and were carefully collected from each phase and analyzed to determine their compositions. The homogeneity of the samples of both phases was maintained using an auxiliary solvent. The addition of an auxiliary solvent prevents phase split after separation.

Analysis. The composition of samples was analyzed by a Varian CP-3800 gas chromatograph (GC) equipped with a thermal conductivity detector (TCD) and Star integrator. High purity helium was used as a carrier gas at a flow rate of 40 $cm^3 \cdot min^{-1}$. A (4 m)·(4 mm) stainless steel column packed with CHROMOSORB T 40 to 60 mesh was used to separate the components. The injection and the detector temperatures were 548.2 K.

The TCD's response was calibrated with *tert*-butanol as an internal standard. The calibration equations were used to convert the area fraction to mole fraction. Calibration coefficients were obtained by fitting a straight line to the calibration results for each composition range. The estimated uncertainty in the mole fraction was about 0.0005. The temperature was estimated to be accurate to within ± 0.1 K.

Results and Discussion

Experimental Data. The experimental tie-line data for the ternary systems of (water + 1,4-butanediol + solvent (cyclohexanol, 2-ethyl-1-hexanol, and 1-decanol) were determined at 298.2 K and atmospheric pressure. The experimental and the correlated tie lines for each ternary system are listed in Table 1. The LLE phase diagrams for these ternary systems were plotted and shown in Figures 1, 2, and 3. Because (1,4-butanediol + water) and (1,4-butanediol + solvent) are two liquid pairs that are completely miscible and the only liquid pair (water + organic solvent) is partially miscible, all three of these ternary systems behave as type-1 LLE.[29] As seen from the LLE phase diagrams, the area of the two-phase region obviously depends on the mutual solubilities of water and the organic solvents. In the ternary systems, water is the most soluble in the system containing cyclohexanol but is the least soluble in 1-decanol or 2-ethyl-1-hexanol. The immiscibility region decreases in the order of the mixtures containing 2-ethyl-1-hexanol (branched aliphatic alcohol) > 1-decanol (linear aliphatic alcohol) > cyclohexanol (cycloaliphatic alcohol). This suggests that the branching on the alcohol solvent molecules increase the immiscibility region.

Correlation Models and Evaluation of the Parameters. The raw experimental LLE data were correlated using the universal quasi-chemical (UNIQUAC) method of Abrams and Prausnitz[27] and the nonrandom two-liquid (NRTL) model of Renon and Prausnitz.[28] The experimental data were then compared with the values correlated by these activity coefficient models.

The observed results were also used to determine the optimum UNIQUAC and NRTL binary interaction parameters between each pair of components in the system. These parameters describe the interaction energy between an $i-j$ pair of molecules or between each pair of compounds. The UNIQUAC structural parameters, r (the number of segments per molecules) and q (the relative surface area per molecules), were computed from the number of molecular groups and the individual values of

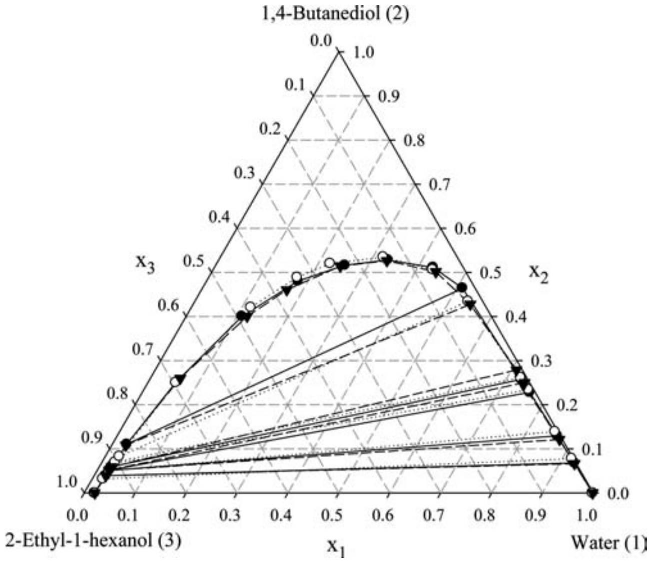

Figure 1. Correlation of the experimental data for (water + 1,4-butanediol + 2-ethyl-1-hexanol) system at 298.2 K: ●, experimental points; ○ UNIQUAC calculated points; ▲, NRTL (α = 0.2) calculated points.

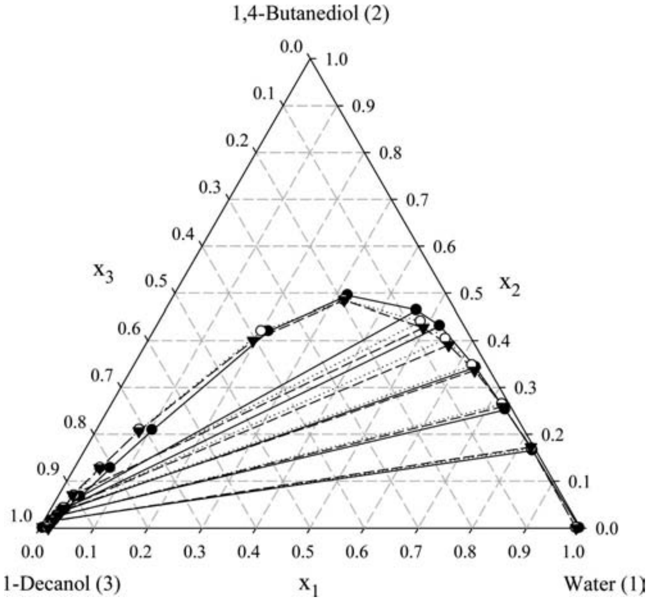

Figure 2. Correlation of the experimental data for (water + 1,4-butanediol +1-decanol) system at 298.2 K: ●, experimental points; ○ UNIQUAC calculated points; ▲, NRTL ($\alpha = 0.2$) calculated points.

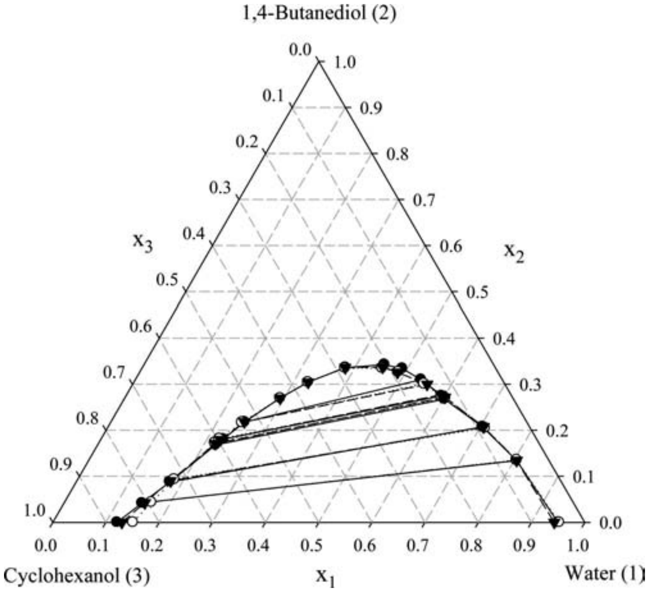

Figure 3. Correlation of the experimental data for (water + 1,4-butanediol + cyclohexanol) system at 298.2 K: ●, experimental points; ○ UNIQUAC calculated points; ▲, NRTL ($\alpha = 0.2$) calculated points.

Table 2. UNIQUAC Structural parameters *r*, *q*

components	*r*	*q*
water	0.9200	1.4000
1,4-butanediol	5.8671	4.8937
2-ethyl-1-hexanol	6.2000	5.1000
1-decanol	7.5007	6.2920
cyclohexanol	4.3489	3.5120

the van der Waals volume and area of the molecule by the Bondi method.[30,31] The detailed description of the meaning of parameters and equations is widely defined in current literature.[32] The values *r* and *q* used in the UNIQUAC equation are presented in Table 2.

Table 3. Correlated Results from the UNIQUAC Model and the Corresponding Binary Interaction Parameters for the Ternary Systems

i-*j*	b_{ij}/K	b_{ji}/K	100·rmsd
Water (1) + 1,4-Butanediol (2) + 2-Ethyl-1-hexanol (3)			
1-2	231.468	−111.271	1.33
1-3	138.033	423.803	
2-3	572.989	−114.689	
Water (1) + 1,4-Butanediol (2) + 1-Decanol (3)			
1-2	605.126	−214.030	1.50
1-3	204.691	257.368	
2-3	753.296	−32.343	
Water (1) + 1,4-Butanediol (2) + Cyclohexanol (3)			
1-2	−97.177	−266.222	0.75
1-3	293.549	−60.670	
2-3	106.424	−334.011	

Table 4. Correlated Results from the NRTL Model and the Corresponding Binary Interaction Parameters for the Ternary Systems

α_{ij}	*i*-*j*	a_{ij}/K	a_{ji}/K	100·RMSD
Water (1) + 1,4-Butanediol (2) + 2-Ethyl-1-hexanol (3)				
0.1	1-2	2873.841	−640.754	1.59
	1-3	2831.117	−440.112	
	2-3	−452.609	2749.998	
0.2	1-2	1955.611	29815.000	1.34
	1-3	2170.733	173.580	
	2-3	49.001	2077.455	
0.3	1-2	1598.319	2416.729	1.42
	1-3	2057.164	515.748	
	2-3	304.243	1632.863	
Water (1) + 1,4-Butanediol (2) + 1-Decanol (3)				
0.1	1-2	1246.550	−401.809	2.07
	1-3	2569.545	−739.638	
	2-3	8328.524	47.517	
0.2	1-2	903.240	2532.549	1.97
	1-3	1959.111	−50.166	
	2-3	4812.550	1379.745	
0.3	1-2	812.183	2143.632	4.22
	1-3	1700.979	293.024	
	2-3	3476.726	1210.883	
Water (1) + 1,4-Butanediol (2) + Cyclohexanol (3)				
0.1	1-2	−2256.100	1344.478	3.65
	1-3	2639.963	−937.049	
	2-3	149.185	−42.502	
0.2	1-2	−243.830	252.622	4.33
	1-3	1779.001	−309.820	
	2-3	−44.198	2007.420	
0.3	1-2	236.584	4173.609	5.71
	1-3	1468.157	−29.081	
	2-3	10.153	1693.104	

The parameters τ_{ij}, τ_{ji}, and α_{ij} are adjustable parameters for each binary pair in the NRTL model. The parameters τ_{ij} and τ_{ji} are related to the characteristic energy of interaction between the molecules of type *i* and *j*, whereas the parameter α_{ij} is related to the nonrandomness of the mixture. In the present work, the value of the nonrandomness parameter, α, was fixed at 0.1, 0.2, and 0.3. Therefore, in this case, for the NRTL model for each possible binary pair in the mixtures, three adjustable parameters are needed.

Tables 3 and 4 show the optimized UNIQUAC and NRTL binary interaction parameters for the ternary systems of (water + 1,4-butanediol) with cyclohexanol, 2-ethyl-1-hexanol, and 1-decanol. The corresponding sets of binary interaction parameters were evaluated by minimizing the square of the differences between the experimental and calculated mole fractions for each of the components over all of the tie lines.

The root-mean-square deviation (RMSD) can be taken to be a measure of the precision of the correlations. The RMSD value was calculated from the difference between the experimental and calculated mole fractions according to the following equation

$$\mathrm{RMSD} = \sqrt{\frac{\sum_{k=1}^{n}\sum_{j=1}^{2}\sum_{i=1}^{3}(x_{ijk} - \hat{x}_{ijk})^2}{6n}} \qquad (1)$$

where n is the number of tie lines, x indicates the experimental mole fraction, $\hat{x}$ is the calculated mole fraction, subscript i indexes components, subscript j indexes phases, and $k = 1, 2, ..., n$ (tie lines). The RMSD percent values in the correlation by UNIQUAC and NRTL models for the ternary systems at 298.2 K are listed in Tables 3 and 4. In general, the average deviations from the UNIQUAC model are smaller than those from the NRTL model.

Distribution Coefficient and Separation Factor. A comparison of the extracting capabilities of the solvents (cyclohexanol, 2-ethyl-1-hexanol, and 1-decanol) was made with respect to distribution coefficients, D, and separation factors, S. The separation factor is defined as the ratio of distribution coefficients of 1,4-butanediol (2) to water (1), $S = D_2/D_1$.

To indicate and compare the ability of the solvents in the recovery of 1,4-butanediol, distribution coefficients for water ($D_1 = x_{13}/x_{11}$) and 1,4-butanediol ($D_2 = x_{23}/x_{21}$) and separation factors were calculated from experimental data. x_{13} and x_{23} are the mole fractions of water and 1,4-butanediol in organic-rich phase, respectively. $x_{11}$and x_{21} are the mole fractions of water and 1,4-butanediol in aqueous phase, respectively. The distribution coefficients and separation factors (extraction power) for the ternary systems are listed in Table 5. For the investigated systems, the experimental results indicate that 2-ethyl-1-hexanol has a much greater separation factor (varying between 4.23 and 23.22) than the others. The range of variation of this quantity for 1-decanol and cyclohexanol is (1.62 to 5.76) and (1.50 to 1.70), respectively. The variation of separation factor of 1,4-butanediol as a function of the mole fraction of the solute in the organic phase for the ternary systems was shown in Figure 4.

Because the low mutual solubility of water and the organic solvents was reliable for extraction of 1,4-butanediol from aqueous solution, the effect of 1,4-butanediol addition on the solubility of water in the organic phase was also investigated at 298.2 K. Figure 5 shows that the solubility of water in the organic phase increases with the amount of 1,4-butanediol added to the water + solvent mixture. However, this is more noticeable in the case of cyclohexanol; the small variation in 2-ethyl-1-hexanol can be seen from the Figure. Because two liquid pairs 1,4-butanediol + water and 1,4-butanediol + solvent are completely miscible, 1,4-butanediol behaves as a common solvent in the water−organic phase mixture.

Table 5. Separation Factors (*S*) and Distribution Coefficients of 1,4-Butanediol (*D*₂) and Water (*D*₁) at 298.2 K

S	D_1	D_2
Water (1) + 1,4-Butanediol (2) + 2-Ethyl-1-hexanol (3)		
23.218	0.0247	0.5727
14.320	0.0274	0.3927
7.252	0.0314	0.2277
6.899	0.0336	0.2315
4.226	0.0562	0.2373
Water (1) + 1,4-Butanediol (2) + 1-Decanol (3)		
5.7625	0.0163	0.0939
4.0452	0.0261	0.1057
2.7319	0.0389	0.1063
1.8563	0.0522	0.0970
1.6179	0.0892	0.1444
Water (1) + 1,4-Butanediol (2) + Cyclohexanol (3)		
1.7020	0.1829	0.3113
1.6972	0.2506	0.4253
1.7050	0.3689	0.6290
1.6933	0.3878	0.6567
1.4976	0.4691	0.7025

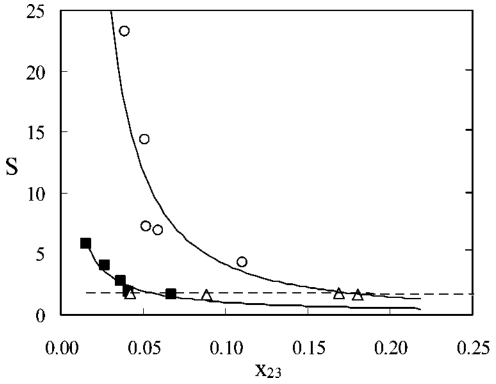

Figure 4. Separation factors versus solubility of 1,4-butanediol in the organic phase at 298.2 K: △, cyclohexanol; ○, 2-ethyl-1-hexanol; ■, 1-decanol.

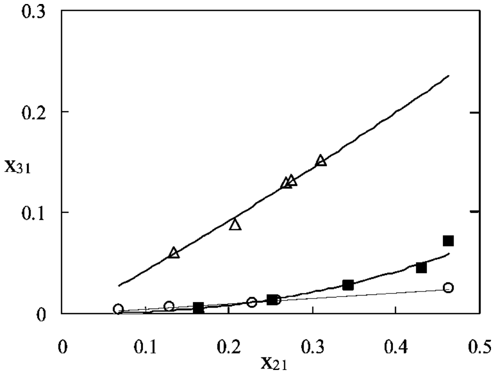

Figure 5. Effects of 1,4-butanediol addition on solubility of water in the organic phase for the investigated ternary systems at 298.2 K: △, cyclohexanol; ○, 2-ethyl-1-hexanol; ■, 1-decanol.

Table 6. Othmer−Tobias and Bachman Equations Constants for the Ternary Systems (Water (1) + 1,4-Butanediol (2) + 2-Ethyl-1-hexanol (3)), (Water (1) + 1,4-Butanediol (2) + 1-Decanol (3)) and (Water (1) + 1,4-Butanediol (2) + Cyclohexanol (3)) at 298.2 K

	Othmer−Tobias correlation			Bachman correlation		
solvents	A	B	R^2	A'	B'	R^2
2-ethyl-1-hexanol	2.2337	−0.4107	0.8712	0.0254	0.3959	0.9941
1-decanol	2.8696	−0.7903	0.9548	0.0109	0.3945	0.9879
cyclohexanol	0.9979	−1.5061	0.9967	0.0219	0.5038	0.9914

The experimental results indicate the superiority of 2-ethyl-1-hexanol as the preferred solvent for the extraction of 1,4-butanediol from its aqueous solutions. The benefit of the branched-chain organic liquids in the solvent extraction has already been reported by Roddy.[33] He 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 improves the distribution coefficient.

The LLE data suggest that 1-decanol may serve as a poor solvent for extracting 1,4-butanediol from its aqueous solutions because it shows a low separation factor. In addition, the separation factor for cyclohexanol is near one, and it shows solubility in water, which means the recovery of 1,4-butanediol by cyclohexanol is impossible. This study also shows that the separation factor values decrease with an increase in the 1,4-butanediol mole fraction in the organic phase for all of the

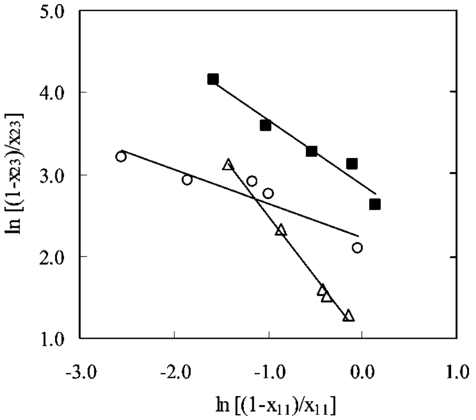

Figure 6. Othmer−Tobias plot for the (water + 1,4-butanediol + solvent) at 298.2 K: △, cyclohexanol; ○, 2-ethyl-1-hexanol; ■, 1-decanol.

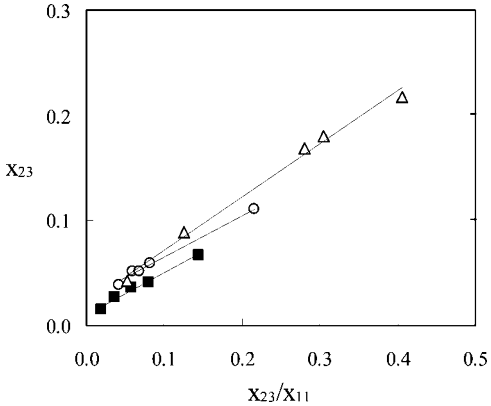

Figure 7. Bachman plot for the (water + 1,4-butanediol + solvent) at 298.2 K: △, cyclohexanol; ○, 2-ethyl-1-hexanol; ■, 1-decanol.

ternary systems here. The solubility of water in organic solvents increases with the addition of 1,4-butanediol to (water + organic solvent) mixtures, as shown in Table 1 and Figures 1, 2, and 3.

Consistency of Tie-Line Data. The consistency of experimental tie-line data can be determined by the Othmer−Tobias[34] and Bachman[35] equations for each solvent, as shown in the following equation

$$\ln\left(\frac{1-x_{23}}{x_{23}}\right)=A+B\ln\left(\frac{1-x_{11}}{x_{11}}\right) \tag{2}$$

$$x_{23}=A'+B'\left(\frac{x_{23}}{x_{11}}\right) \tag{3}$$

where x_{11} is the mole fraction of water in aqueous phase and x_{23} is the mole fraction of 1,4-butanediol in organic phase (extracted phase). A, B, A', and B' are the parameters of the Othmer−Tobias and the Bachman correlations, respectively.

The parameters of the Othmer−Tobias and Bachman correlations are listed in Table 6 at T = 298.2 K. For these investigated systems, the Othmer−Tobias and Bachman plots are also shown in Figures 6 and 7, respectively. The correlation factor (R^2) is approximately unity, and the linearity of the plots indicate the degree of consistency of the measured LLE data in this study.

Conclusions

The LLE data for the ternary systems of (water + 1,4-butanediol + 2-ethyl-1-hexanol), (water + 1,4-butanediol + 1-decanol), and (water + 1,4-butanediol + cyclohexanol) were studied at 298.2 K. Each ternary system exhibits type-1 behavior of LLE.

The UNIQUAC and NRTL (α = 0.2) solution models were satisfactorily used to correlate the experimental LLE results and to calculate the phase compositions of the studied mixtures. The corresponding optimized binary interaction parameters were also calculated. The UNIQUAC method gives better results than the NRTL model for the three investigated systems. In general, the average deviations from the UNIQUAC model are smaller than those from the NRTL model. The average RMSD value between the observed and calculated mole fractions for the UNIQUAC model varies between 0.75 and 1.50.

The separation factor and distribution coefficient for each of organic solvent used in this work were calculated and compared. In the extraction of 1,4-butanediol from water, the solvent with the higher selectivity and distribution coefficient is preferred. The experimental results indicate the superiority of 2-ethyl-1-hexanol as the preferred solvent for the extraction of 1,4-butanediol from its aqueous solutions.

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