Influence of the Temperature on the Liquid−Liquid−Solid Equilibria of the Ternary System Water + Ethanol + 1-Decanol

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Liquid−liquid equilibrium data for the ternary system water + ethanol + 1-decanol have been measured at (2, 15, and 25) °C, with two different methods of analysis: refractive index and gas chromatography. A small region with three phases (solid−liquid−liquid) and two regions with two phases (solid−liquid) appear at 2 °C. Liquid−liquid regions show quite similar shapes at all of the temperatures.

Introduction

Ethanol is increasingly being used as a large-scale fuel, but ethanol produced using conventional processes of batch fermentation of sugars with yeast, followed by distillation to recover the ethanol, is uneconomical as a fuel, compared to fossil fuels,[1,2] although this assertion could be discussed. Therefore, an objective of science should be to achieve a lower economic cost process in the extraction of ethanol from an aqueous solution, obtained in the fermentation of carbohydrates. One of the possibilities is the application of long-chain alcohols, particularly the alcohols that exist in nature, for instance, 1-dodecanol[3] or 1-decanol, to accomplish an improvement in the separation process of ethanol.

In previous works, different liquid−liquid[4−6] and solid−liquid−liquid equilibria[3] were studied as a means to perform a better separation. The design equipment calculations of each process were carried out, and the properties that these solvents could offer to decrease the energetic requirements of the extraction process were studied.

1-Decanol is another long-chain alcohol that exists in nature. Its melting temperature is 6.6 °C, and it is possible to carry out an extraction with solid 1-decanol, at a temperature below 6.6 °C or with liquid 1-decanol at a temperature above this. The liquid−liquid equilibria of the ternary system of water + ethanol + 1-decanol has already been made at 30 °C,[7] but to study the influence of the temperature on the binodal curve and on tie lines, equilibria for the ternary system water + ethanol + 1-decanol at temperatures of (2, 15, and 25) °C are reported.

Experimental Section

Ethanol and 1-decanol were supplied from Merck with a stated mass fraction purity of 99.8 % and 99 %, respectively. No further purification was made. The water used was purified using a Milli Q-Plus system.

Solubility data of liquid−liquid and solid−liquid−liquid equilibrium systems were determined at (2, 15, and 25) °C by titration using the cloud point method. After reaching the end point of the titration, the refractive index measurement to the homogeneous mixtures was done. Samples were heated to (25 ± 0.01) °C, to avoid phase splitting during their refractive index measurement, which was carried out with an automatic refractometer (Leica AR600, accuracy ± 0.00002). A graph of refractive index (at 25 °C) versus ethanol composition (of points belonging to the solubility curve) was prepared for each temperature of study: (2, 15, and 25) °C.

Equilibrium data were obtained by preparing mixtures of known overall mass composition, by weighing the constituents. In the solid−liquid−liquid equilibrium at 2 °C, it was observed during the experiment that the precipitation of solid 1-decanol from a liquid phase, as a consequence of decreasing temperature, produced a gel that made the separation of phases difficult. However, if equilibrium was reached starting from a temperature lower than the equilibrium temperature, no gel was formed, and the liquid and solid phases were easily separable as occurred with 1-dodecanol.[3] Therefore, the components were weighed and mixed at a temperature lower than the equilibrium temperature and introduced into a thermostatic bath at this temperature. Consequently, equilibrium was reached from the dissolution of 1-decanol instead of precipitation of it.

The prepared mixtures were stirred with a magnetic stirrer for at least two weeks at a constant temperature to ensure that equilibrium was reached, since dissolution of the long-chain alcohols is low and not very fast at the operating temperatures. The phases were then allowed to settle and separate, and samples were taken from the liquid phases using syringes.

Two different analytical methods were used to determine the compositions of the samples. First, equilibrium data for the three temperatures were measured with the refraction index method, as in the previous paper for 1-dodecanol.[3] Analyses of the equilibrium phases were carried out by heating each separated phase at 25 °C, and then the refraction indexes were measured. The values obtained, interpolated in the refractive index versus ethanol composition solubility curve, provide sufficient information to determine each tie line. Furthermore, the water concentration in the organic phase was measured and checked with the Karl Fischer method using a Mettler DL18 titrator.

The second analytical method used was by gas chromatography, and this was used to determine equilibrium data at (2 and 25) °C, to achieve more accurate results and compare them with the refraction index measurement. Shimadzu GC-14A gas chromatography equipment coupled to a personal computer employing Shimadzu Labsolution GC-Solution software was utilized. The separation of the components was carried out in a

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Table 1. Ternary Mutual Solubility Data (Mass Fraction) for Water (1) + Ethanol (2) + 1-Decanol (3) at (2, 15, and 25) °C

100 w_1	100 w_2	100 w_3
	$t = 2$ °C	
3.75	6.11	90.1
5.08	9.41	85.5
7.87	24.0	68.1
16.1	35.0	48.9
24.8	40.4	34.8
35.2	45.3	19.5
54.1	43.8	2.13
56.5	42.5	1.02
	$t = 15$ °C	
3.64	0.00	96.4
4.02	6.92	89.1
5.93	14.1	80.0
10.2	24.7	65.1
18.9	35.1	46.0
24.8	41.0	34.1
36.7	43.1	20.1
48.9	42.8	8.33
55.6	41.7	2.67
	$t = 25$ °C	
3.47	0.00	96.5
3.67	7.16	89.2
6.30	15.1	78.6
13.5	32.3	54.2
24.0	41.2	34.7
34.9	41.9	23.2
49.4	41.6	8.97
55.8	40.6	3.61

2 m × 3 mm column packed with Porapak Q 80/100. The oven temperature was 240 °C, and the helium flow rate was 50 mL·min^{-1}.

Detection was carried out by various techniques, which depend on the composition of the samples. A thermal conductivity detector (TCD) was used for all compounds (water, ethanol, and 1-decanol), except for 1-decanol in the aqueous phase, which was analyzed with the flame ionization detector (FID). The temperature of the detector was 250 °C, and the current intensity on the TCD was 100 mA. An internal standard was used to obtain quantitative results from the analysis of the liquid phases. For this reason, 1-propanol, which is completely miscible in water, ethanol, and 1-decanol, was also added to the sample vials. Moreover, the addition of the standard prevents phase splitting when adjusting the temperature after separation of the phases.

The relative uncertainty of the mass fraction measurements was approximately 2 %, calculated by the analysis of prepared standards. The compositions obtained with their relative uncertainty and the known overall compositions of the heterogeneous mixture were used to check the mass balance and fit the results following a data reconciliation method.[8] This method was developed to check and fit liquid−liquid equilibrium data obtained experimentally. The analytical concentrations are changed slightly within the interval given by the uncertainties of the determinations to satisfy the material balances. The method consists of a minimization with constraints of a proposed objective function. The results reported here correspond to the values obtained by this method.

Results

Table 1 presents the experimental solubility data obtained for each system. Stephenson and Stuart[9] reported data on the mutual solubility of water and 1-decanol at temperatures between (19.8 and 90.4) °C. Their data at (19.8 and 29.6) °C (100 w (H_2O) = 3.68 and 3.35 in 1-decanol, respectively) agree with that reported in this paper at (15 and 25) °C (100 w (H_2O) = 3.64 and 3.47 in 1-decanol, respectively).

Table 2. Tie-Line Data (Mass Fraction) for Water (1) + Ethanol (2) + 1-Decanol (3) at (2 and 25) °C[a]

aqueous phase			organic phase		
100 w_1	100 w_2	100 w_3	100 w_1	100 w_2	100 w_3
		$t = 2$ °C			
		One Liquid Phase + One Solid Phase (1-Decanol)			
				4.12	95.9
		Two Liquid Phases + One Solid Phase (1-Decanol)			
94.3	5.69	< 0.15	4.42	1.07	94.5
		Two Liquid Phases			
57.9	41.4	0.71	22.3	39.5	38.2
66.8	33.2	< 0.15	11.1	27.6	61.3
75.1	24.7	< 0.15	6.28	15.1	78.6
85.5	14.3	< 0.15	5.02	5.54	89.4
		$t = 25$ °C			
		Two Liquid Phases			
55.6	40.1	4.33	25.2	39.4	35.2
62.1	37.5	0.47	19.0	33.6	47.4
67.0	32.9	0.15	12.2	27.5	60.3
76.5	23.5	< 0.15	7.46	16.9	75.6
87.4	12.6	< 0.15	5.04	7.52	87.4
100.0		< 0.15	2.68		97.3

[a] Compositions determined by gas chromatography.

Table 3. Tie-Line Data (Mass Fraction) for Water (1) + Ethanol (2) + 1-Decanol (3) at 15 °C[a]

aqueous phase			organic phase		
100 w_1	100 w_2	100 w_3	100 w_1	100 w_2	100 w_3
		Two Liquid Phases			
57.8	40.9	1.56	22.8	39.3	38.0
66.1	33.9	< 0.15	10.8	26.6	62.5
74.9	25.2	< 0.15	6.47	15.4	79.0
85.8	14.3	< 0.15	4.26	5.93	90.0
100	0.00	< 0.15	3.34	0.00	96.7

[a] Compositions determined with the refraction index technique.

With respect to the equilibrium data, Tables 2 and 3 show tie-line data for water (1) + ethanol (2) + 1-decanol (3), at the three different temperatures. The results obtained at (2 and 25) °C with gas chromatography agreed perfectly with those obtained using the refraction index technique, and for this reason only the results with gas chromatography for (2 and 25) °C are presented in Table 2. Furthermore, the differences between the results at (25 and 15) °C are very small, and consequently the analysis of the compositions of the tie lines at 15 °C which had been obtained with the refraction index technique (Table 3) was not repeated using the other method.

The phase diagrams for these systems are shown in Figures 1 to 3. As can be seen in the figures, at 2 °C the ternary system presents four heterogeneous regions: two small regions with two phases (solid−liquid), a very small region with three phases (solid−liquid−liquid), and a large region with two phases (liquid−liquid). When the temperature increases above 2 °C, the phase diagram only presents a heterogeneous region that contains two liquid phases, as can be observed at (15 and 25) °C. As shown in Figure 3, tie lines reported in this work at 25 °C agree with those reported by Kirbaslar et al.[7] at 30 °C, although the tendency of the slopes of their tie lines is not very consistent.

The universal quasichemical activity coefficient (UNIQUAC) model was used to correlate simultaneously the results obtained at the three temperatures. Table 4 shows the obtained parameters and the mean deviations of the correlation. Figures 1 and 2 show the tie lines calculated compared with the experimental ones.

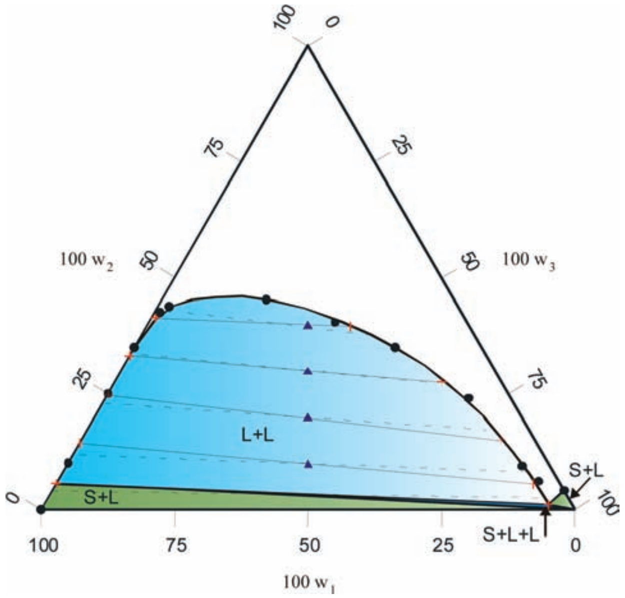

Figure 1. Solid−liquid−liquid and liquid−liquid equilibria for the ternary system water (1) + ethanol (2) + 1-decanol (3) at 2 °C. ●, experimental solubility; ▲, overall mass composition; − +, experimental tie lines; − −, UNIQUAC tie lines.

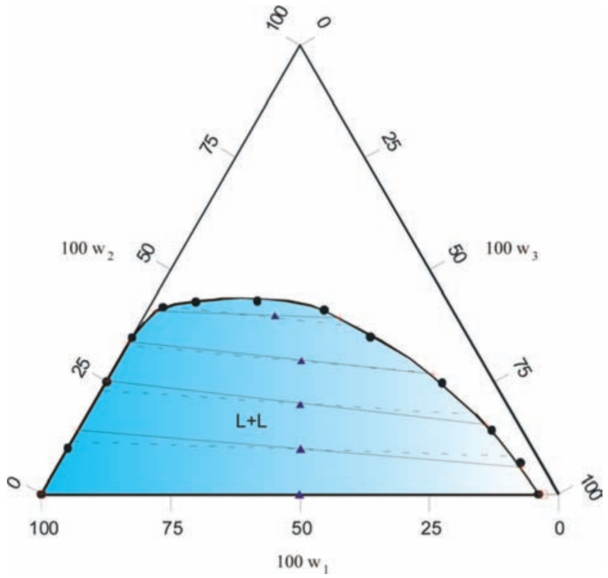

Figure 2. Solid−liquid−liquid and liquid−liquid equilibria for the ternary system water (1) + ethanol (2) + 1-decanol (3) at 15 °C. ●, experimental solubility; ▲, overall mass composition; − +, experimental tie lines; − −, UNIQUAC tie lines.

On the other hand, tie lines obtained in this work show that the percentage of ethanol is greater in 1-decanol than in 1-dodecanol,[3] as can be seen in the different slopes of the tie-line data. Distribution coefficients, d_i, for water ($i = 1$) and ethanol ($i = 2$), and separation factors, s, were calculated as follows:

$$d_i = w_{i3}/w_{i1}$$

$$s = \frac{\text{distribution coefficient of ethanol}}{\text{distribution coefficient of water}} = \frac{w_{23}/w_{21}}{w_{13}/w_{11}}$$

where w_{23} and w_{21} are the ethanol mass fractions in solvent-rich and water-rich phases, respectively, and w_{13} and w_{11} are the water mass fractions in solvent-rich and water-rich phases, respectively. The results are shown in Table 5.

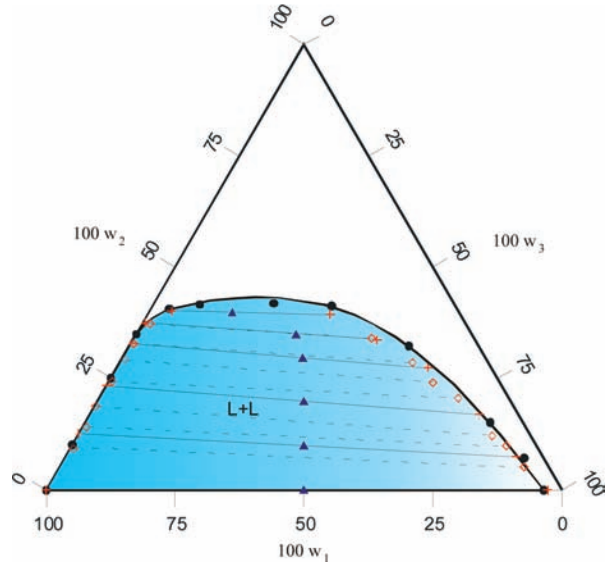

Figure 3. Solid−liquid−liquid and liquid−liquid equilibria for the ternary system water (1) + ethanol (2) + 1-decanol (3) at 25 °C. ●, experimental solubility; ▲, overall mass composition; − +, experimental tie lines; − −, Kirbaslar tie lines, − − ◇.

Table 4. UNIQUAC Binary Interaction Parameters ($J \cdot mol^{-1}$) and Deviations between Experimental and Calculated Mole Fractions

		A_{ij} $J \cdot mol^{-1}$	A_{ji} $J \cdot mol^{-1}$
water	ethanol	2603.82	−2308.30
water	1-decanol	1752.97	2027.82
ethanol	1-decanol	−1382.21	759.91

	water aq.	ethanol aq.	water org.	ethanol org.
mean deviation	0.0147	0.0128	0.0354	0.0112
max. deviation	0.0359	0.0259	0.0733	0.0277

Table 5. Mass Fraction of Ethanol in the Aqueous Phase (w_{21}), Distribution Coefficient (d_2), and Separation Factors (s) for the System Water (1) + Ethanol (2) + 1-Decanol (3)

100 w_{21}	d_2	s
	$t = 2$ °C	
41.4	0.95	2.48
33.2	0.83	4.99
24.7	0.61	7.30
14.3	0.38	6.60
	$t = 15$ °C	
40.9	0.96	2.44
33.9	0.78	4.80
25.2	0.61	7.06
14.4	0.41	8.32
	$t = 25$ °C	
40.1	0.98	2.17
37.5	0.90	2.94
32.9	0.84	4.56
23.5	0.72	7.40
12.6	0.60	10.4

Conclusion

The changes in the shape of the equilibrium diagram can be used to improve the process of extraction of ethanol from aqueous solutions using 1-decanol as a solvent. The effectiveness of extraction of ethanol by 1-decanol is given by its separation factor, which is an indication of the ability of 1-decanol to separate ethanol from water. This quantity is found to be greater than 1, which means that extraction of ethanol by 1-decanol is possible.

The separation factors are not constant over the whole two-phase region, as shown in Table 5 for each temperature. Although the separation factors of ethanol are not very high (between 2.2 and 10.4), the combination of melting and solidification of 1-decanol in this range of temperature could improve the economic aspects of the extraction, and the solvent could be recovered via crystallization with an important saving in the cost of the process.

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