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Influence of the Temperature on the Liquid−Liquid Equilibrium of the Ternary System 1-Pentanol + 1-Propanol + Water

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Liquid−liquid equilibrium data for the ternary system 1-pentanol + 1-propanol + water have been determined experimentally at (25, 50, 85, and 95) °C. The results have been correlated simultaneously by the UNIQUAC method, obtaining a set of interaction parameters valid over the temperature range of the experimental results.

1. Introduction

As has been stated in recent papers,[1,2] the correlation of the liquid−liquid equilibrium data is currently done by fitting each set of isothermic data separately. To obtain an unique set of parameters valid for the range of temperatures studied, a simultaneous correlation of experimental liquid−liquid data, using the UNIQUAC[3] model for the ternary system 1-pentanol + 1-propanol + water at temperatures ranging from 25 °C to 95 °C was made.

2. Experimental Section

2.1. Chemicals. Bidistilled water was used. 1-Pentanol (Panreac), 1-propanol (Merck), and 2-propanol (Panreac) had the nominal purities >99.0, >99.5, and >99.8 mass %, respectively. The first two were used as components, and 2-propanol was used as the internal standard. Prior to measurements, chemical purities were checked with gas−liquid chromatography.

2.2. Equilibrium Measurements. The procedure is the same as that previously presented in the literature.[1,2] Measurements were made at four temperatures. Equilibrium data were obtained by preparing mixtures of known overall composition by mass followed by intense stirring and setting for at least 4 h at constant temperatures: (25 ± 0.1) °C, (50 ± 0.1) °C, (85 ± 0.1) °C, and (95 ± 0.1) °C. Liquid mixtures were prepared in test tubes which were filled almost completely. The reason for this is to prevent the appearance of an additional and important vapor phase, liable to happen when working at high temperatures. At the end of the setting period, samples were taken from both phases and analyzed by gas chromatography (Shimadzu chromatograph GC-14A equipped with an electronic integrator, Shimadzu C-R6A Chromatopac, and an automatic injector, Shimadzu AOC-14). Good separation of the four components (three corresponding to the equilibrium and the fourth, the internal standard) was obtained on a 2 m × 1/8 in. column packed with Porapak Q-S 80/100. The column temperature was 180 °C, and detection was carried out by different techniques depending on the compositions of the samples: TCD for rich organic samples and FID for rich water samples. For TCD the detector current was 100 mA. The helium flow rate was adjusted to 30 mL/min. To obtain quantitative results, the internal standard method was applied using 2-propanol.

Table 1. Tie-Line Data (x_i Mole Fraction) for 1-Pentanol (1) + 1-Propanol (2) + Water (3)

aqueous phase		organic phase		aqueous phase		organic phase	
$100x_1$	$100x_2$	$100x_1$	$100x_2$	$100x_1$	$100x_2$	$100x_1$	$100x_2$
			t = 25 °C				
0.40	0	63.5	0	0.39	3.78	17.2	25.5
0.42	1.53	41.2	15.3	0.51	5.18	10.4	24.3
0.39	2.67	27.2	23.0	0.71	6.34	6.93	21.7
			t = 50 °C				
0.40	0	61.6	0	0.35	2.21	25.9	21.5
0.37	0.67	51.5	7.76	0.35	2.79	21.7	23.8
0.37	1.23	41.1	13.9	0.38	3.37	17.3	25.1
0.35	1.86	33.7	18.3	0.53	4.17	12.4	24.2
			t = 85 °C				
0.42	0	60.0	0	0.46	1.87	25.8	18.6
0.43	0.58	46.5	8.24	0.57	2.89	16.6	20.1
0.39	1.15	36.4	14.5	0.98	4.73	8.21	17.3
			t = 95 °C				
0.42	0	56.5	0	0.50	1.95	24.0	17.4
0.44	0.66	42.1	8.24	0.52	2.75	14.5	18.1
0.47	1.19	32.9	13.5				

The results of the concentrations of the three components of both conjugated phases, and the data of the initial composition mixture were used to check the mass balance and fit the results following a method of data reconciliation.[4] The relative accuracy allowed for the mole fraction measurements was 2%. The results reported correspond to the values obtained using this method.

3. Results and Discussion

Tie-line data at different temperatures at atmospheric pressure are presented for the ternary system 1-pentanol + 1-propanol + water in Table 1. The results are also graphically presented in Figure 1. Since the information is related to a relatively small area, only the relevant part of the triangle diagram is presented in the figure, where the information of the tie lines can be observed, for all the temperatures studied, as points joined by a solid line.

In Figure 2 the four piled diagrams can be observed, the vertical coordinate being the temperature, for the purpose of spatially observing the effect of temperature on the heterogeneous phase.

In both figures it can be observed that a decrease in the size of the heterogeneous region with an increase in temperature is not very important.

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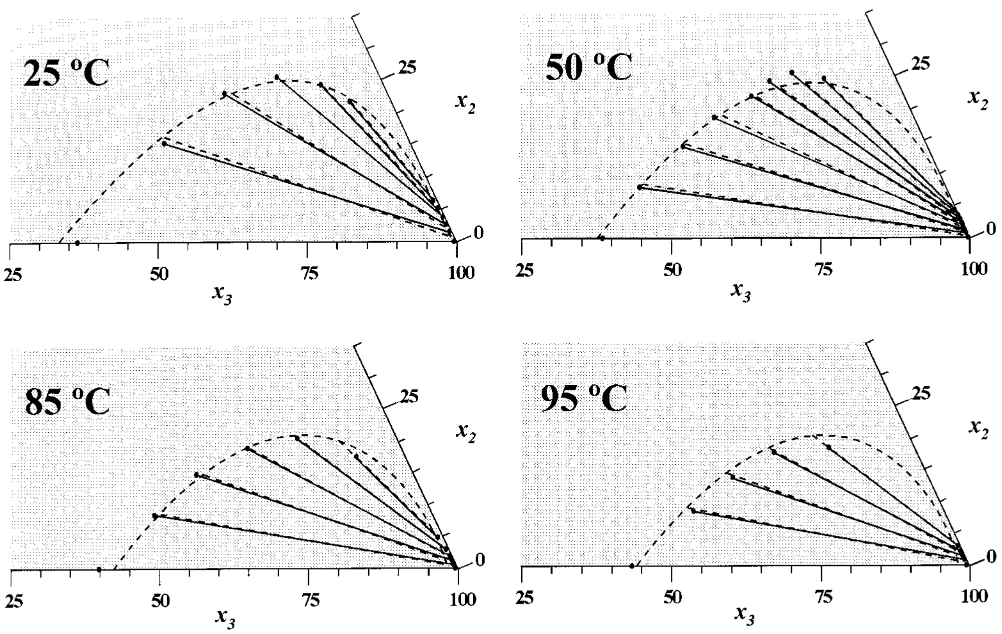

Figure 1. Liquid−liquid equilibrium data of the system 1-pentanol (1) + 1-propanol (2) + water (3) at different temperatures: continuous line, experimental data; dashed line, UNIQUAC correlation data.

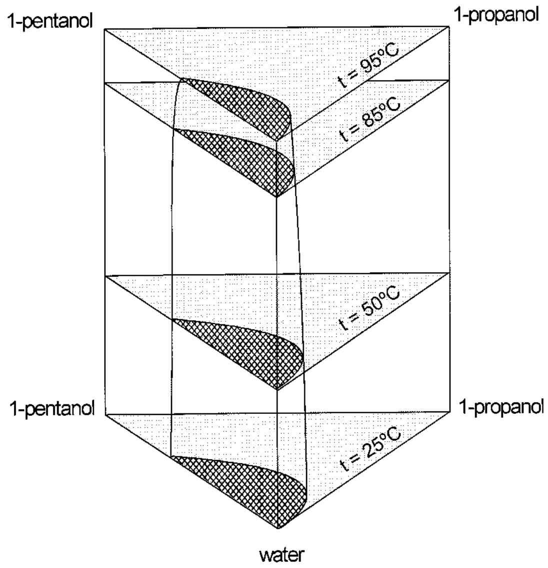

Figure 2. Phase equilibrium diagram for the system 1-pentanol (1) + 1-propanol (2) + water (3) in the temperature range 25−95 °C.

4. Correlation of the Experimental Data

As in previous papers,[1,2] the UNIQUAC model was used to correlate the experimental liquid−liquid equilibrium data. The pure component molecular structure constants for the UNIQUAC equation are those given by Sorensen and Arlt.[5] The parameter estimation procedure and the objective function used are described elsewhere.[6] The goodness of fit was calculated in terms of the root-mean-square (rms) deviation in phase composition

$$F = \mathrm{rms} = \Big(\sum_{k}^{M}\sum_{j}^{2}\sum_{i}^{3}(x_{ijk} - \hat{x}_{ijk})^2/6M\Big)^{1/2} \qquad (1)$$

where M is the number of tie lines, x indicates the experimental mole fraction, $\hat{x}$ are the calculated mole fractions, and the subscript i indexes the components, j the phases, and k the tie lines

Table 2. Optimized UNIQUAC Binary Interaction Parameters a_{ij}/K Valid for the Range of Temperature Considered

a_{12}	497.997	a_{21}	−360.400
a_{13}	133.628	a_{31}	176.626
a_{23}	−185.127	a_{32}	406.747
rms deviation		0.0106	

The simultaneous correlation of all the experimental liquid−liquid data of the system was performed in order to obtain a unique set of parameters valid for the range of temperatures studied. Table 2 lists the optimized UNIQUAC binary interaction parameters a_{ij} in K, obtained in a simultaneous correlation of all data assuming that their dependence on temperature is negligible. The obtained rms deviation of 0.0106 is of the composition in molar fraction. The comparison between experimental (solid lines) and calculated data using these parameters (dotted lines) is presented in Figure 1.

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