Isobaric Vapor−Liquid Equilibria for the System 1-Pentanol + Ethanol + Water at 101.3 kPa

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Consistent vapor−liquid equilibrium data for the ternary system 1-pentanol + ethanol + water are reported at 101.3 kPa at temperatures in the range 353 to 393 K. The VLE data were satisfactorily correlated with the UNIQUAC model.

1. Introduction

Distillation is the most common operation in the chemical industry used for the separation of liquid mixtures. The optimal design of distillation columns requires the availability of accurate vapor−liquid equilibria (VLE) data and the use of generalized methods to predict the properties of the mixtures. Experimental measurements of vapor−liquid equilibria for ternary or higher mixtures are quite scarce due to the experimental effort necessary to obtain a complete description of the system.

This paper reports the results of measurements of vapor−liquid equilibria for the system 1-pentanol + ethanol + water at atmospheric pressure. This system could be interesting for testing models of association. No relevant measurements of vapor−liquid equilibria for this system have previously been reported. We have found one work[1] with a few tie lines at 97.86 kPa, in a very narrow region where pentanol content was always <0.007 mol % in the liquid phase and the corresponding vapor concentration values were <0.03 mol %.

2. Experimental Section

2.1. Chemicals. Bidistilled water was used. 1-Pentanol (Panreac), ethanol (Merck), and 1-propanol (Merck) had nominal purities >99.0, >99.8, and >99.5% by mass, respectively. The first two were used as components, and 1-propanol was used as the internal standard. All of them were used as supplied after chromatography failed to show any significant organic impurities. A Karl Fischer method was used to determine that the water content in the alcohols was negligible (<0.2% by mass).

2.2. Apparatus and Procedure. The vessel used in this work was an all glass, dynamic recirculating still described elsewhere,[2] equipped with a Cottrell pump. The still (Labodest model) manufactured by Fischer Labor und Verfahrenstechnik (Germany) is capable of handling pressures from 0.25 to 400 kPa and temperatures up to 523.15 K. The Cottrell pump ensures that both liquid and vapor phases are in intimate contact between them and with the sensor element. The equilibrium temperature was measured with a Fisher digital thermometer provided with a 2-mm diameter Pt-100 temperature sensor with an accuracy of ±0.1 K. The pressure was measured with a digital manometer with an accuracy of ±0.01 kPa.

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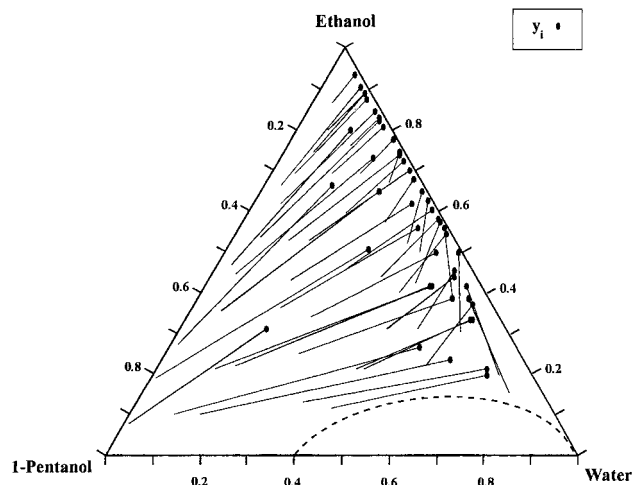
Figure 1. Vapor−liquid equilibrium tie lines for the 1-pentanol + ethanol + water system at 101.3 kPa: (●) vapor-phase mole fractions.

In each experiment, after the pressure was fixed, the heating and shaking system of the liquid mixture was turned on. The still was operated until equilibrium was reached. Equilibrium conditions were assumed when temperature and pressure remained constant for at least 30 min. After this time, 0.5 mL samples of liquid and condensed vapor phases were taken with syringes without disruption of the operation. An internal standard was added to each sample for the analytical determination.

All the samples were analyzed by means of 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 (including the internal standard) was obtained on a 2 m by 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 composition of the samples: TCD for organic-rich samples (analyzing water, 1-pentanol, and ethanol) and FID for water-rich samples (analyzing 1-pentanol and ethanol). In this case, the water content was inferred from a mass balance. For TCD the detector current was 100 mA. The helium flow rate was adjusted to 30 mL·min^{−1}. To obtain quantitative results, the internal standard method was applied. The standard compound

Table 1. Vapor−Liquid Equilibrium Data for the System 1-Pentanol (1) + Ethanol (2) + Water (3) at 101.3 kPa[a]

T/K	x_1	x_2	y_1	y_2
393.35	0.914	0.075	0.509	0.309
376.55	0.716	0.268	0.196	0.657
365.85	0.503	0.465	0.085	0.796
358.95	0.301	0.661	0.014	0.900
353.55	0.092	0.865	0.009	0.932
354.55	0.136	0.793	0.012	0.888
355.75	0.193	0.739	0.012	0.886
357.55	0.256	0.691	0.014	0.870
359.65	0.324	0.617	0.013	0.842
361.75	0.412	0.530	0.014	0.820
364.95	0.506	0.441	0.074	0.725
368.65	0.583	0.351	0.101	0.644
378.65	0.803	0.184	0.194	0.502
370.65	0.667	0.207	0.104	0.413
362.85	0.452	0.363	0.062	0.558
361.15	0.394	0.431	0.049	0.617
358.55	0.309	0.526	0.010	0.696
355.95	0.198	0.590	0.015	0.717
353.35	0.071	0.667	0.010	0.741
354.95	0.103	0.520	0.010	0.645
357.35	0.203	0.432	0.009	0.578
353.75	0.107	0.755	0.012	0.824
355.45	0.181	0.689	0.015	0.801
359.95	0.352	0.527	0.013	0.737
378.00	0.805	0.100	0.206	0.264
375.25	0.752	0.098	0.158	0.233
368.90	0.616	0.221	0.106	0.416
354.15	0.117	0.688	0.010	0.771
356.45	0.136	0.420	0.010	0.569
355.05	0.129	0.569	0.013	0.676
357.95	0.260	0.456	0.011	0.602
361.65	0.399	0.337	0.055	0.493
364.15	0.467	0.250	0.076	0.384
366.65	0.522	0.124	0.088	0.211
365.85	0.469	0.115	0.095	0.196
362.70	0.368	0.207	0.063	0.328
360.00	0.256	0.306	0.046	0.435
357.50	0.183	0.396	0.009	0.541
355.05	0.090	0.491	0.010	0.621
356.05	0.072	0.390	0.008	0.554
358.95	0.188	0.306	0.039	0.452
362.35	0.351	0.208	0.063	0.328
360.75	0.215	0.217	0.043	0.364
357.45	0.100	0.303	0.006	0.496
359.15	0.071	0.193	0.033	0.414
359.95	0.070	0.153	0.043	0.382

[a] x_i is the liquid-phase mole fraction, and y_i is the vapor-phase mole fraction.

Table 2. Optimized UNIQUAC Binary Interaction Parameters a_{ij}/K for the VLE Data of the System 1-Pentanol (1) + Ethanol (2) + Water (3)

$a_{12} = 263.843$	$a_{21} = -142.142$
$a_{13} = 424.638$	$a_{31} = -46.081$
$a_{23} = 103.360$	$a_{32} = 38.767$

used for this purpose was 1-propanol. The standard deviation in the mole fraction was usually <0.001.

3. Results and Discussion

Isobaric VLE data were determined for the totally miscible mixtures of the three components. The experimentally determined compositions of the liquid and vapor phases, and the corresponding equilibrium temperatures, are listed in Table 1 and depicted in Figure 1. The binodal curve data (dashed line) shown in Figure 1 are taken from a previous work[3] and mark the miscibility limit of the three liquid components at 358.15 K. The reason for having selected this temperature value is because it is closer to the bubble point of the mixtures presented in Table 1.
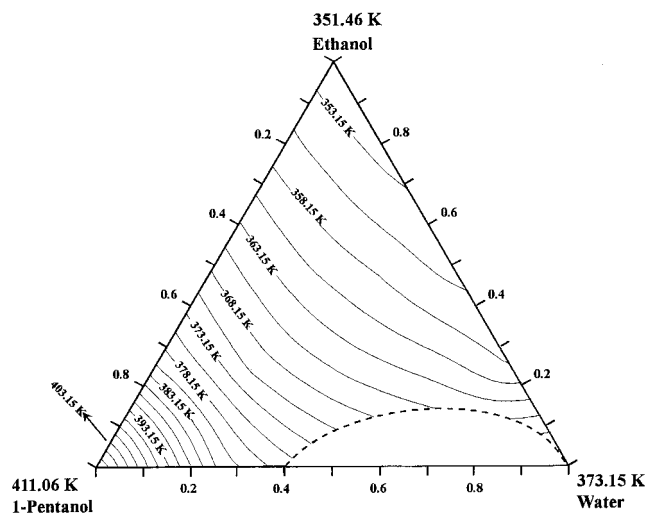
Figure 2. Vapor−liquid isotherms for the ternary system 1-pentanol + ethanol + water at 101.3 kPa calculated with the UNIQUAC equation, as a function of the liquid mole fraction.
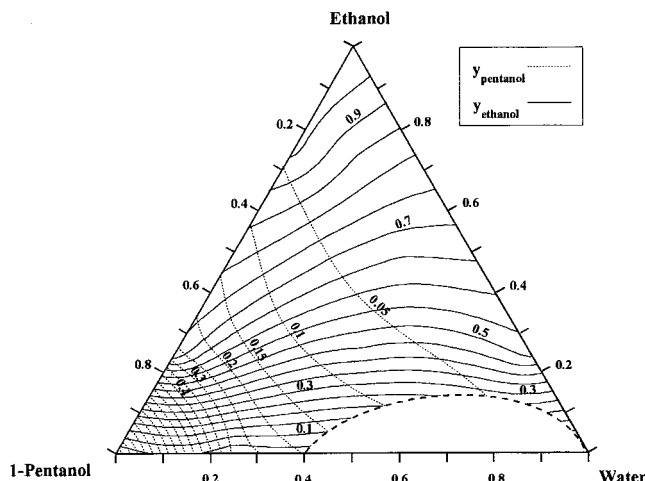
Figure 3. Vapor-phase composition for the ternary system 1-pentanol + ethanol + water at 101.3 kPa calculated with the UNIQUAC equation, as a function of the liquid mole fraction; the basic grid represents the liquid composition (x_i); the parametric curves indicate equilibrium vapor mole fractions of 1-pentanol (· · ·) and ethanol (−).

The ternary data were found to be thermodynamically consistent, as tested by the point to point $L - W$ method of Wisniak.[4] All the values of $D = 100(L - W)/(L + W)$ were <3. Vapor pressures were calculated with the Antoine equation, whose parameters A_i, B_i, and C_i for 1-pentanol, ethanol, and water were taken from the literature.[5]

The UNIQUAC equation was used to correlate the experimental data. The pure component molecular structure constants for the UNIQUAC equation were those given by Sorensen and Arlt.[6] An ideal vapor phase was assumed. For the purpose of the fitting the parameters, a nonlinear optimization method was used to minimize the following objective function:

$$OF = 1000\Sigma\left(\frac{P_{exp} - P_{cal}}{P_{exp}}\right)^2 + \Sigma\left(\frac{\gamma_{exp} - \gamma_{cal}}{\gamma_{exp}}\right)^2 \quad (1)$$

where P is the pressure and γ the liquid-phase activity coefficient.

Table 2 lists the optimized UNIQUAC binary interaction parameters a_{ij} in K obtained.

Mean absolute deviations between experimental and calculated vapor-phase mole fractions and pressures were $MAD(y_{water}) = 0.05$, $MAD(y_{ethanol}) = 0.03$, and $MAD(P) = 1.7$ kPa. The model represents the experimental data successfully. The model parameters can be used to predict boiling points and vapor-phase compositions from the liquid-phase composition at the system pressure. Figure 2 shows the isotherms of the ternary system as a function of liquid mole fraction. In Figure 3, the mole fraction of component i in the liquid, x_i, is represented by the basic grid, and the vapor mole fraction, y_i, in equilibrium with the liquid is shown as parametric curves.

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