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Liquid−Liquid Equilibria for 2-Ethoxyethanol + Water + *n*-Alkane + Benzene at 293.15 K

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Liquid−liquid equilibrium data were measured at 293.15 K for three quaternary systems: 2-ethoxyethanol + water + hexane + benzene, 2-ethoxyethanol + water + heptane + benzene, and 2-ethoxyethanol + water + octane + benzene. The nonrandom two-liquid equation was used to correlate the experimental data, and the root-mean-square deviations are shown.

Introduction

2-Ethoxyethanol (2-EE), an important industrial chemical, is of interest because of its application as a solvent, a solubilizing agent in many industries, and a liquid fuel additive. A survey of the literature showed that thermodynamic properties and liquid−liquid equilibrium (LLE) data for binary mixtures containing 2-ethoxyethanol have been reported by several authors.[1−4] In this paper, we present new experimental quaternary liquid−liquid equilibria for 2-ethoxyethanol + water + hexane + benzene, 2-ethoxyethanol + water + heptane + benzene, and 2-ethoxyethanol + water + octane + benzene at 293.15 K. The weight percent of water in 2-ethoxyethanol was 10 mass % for all systems studied. Further, the experimental quaternary results were correlated by fitting the nonrandom two-liquid (NRTL) model.[5]

Experimental Section

Materials. 2-Ethoxyethanol, hexane, heptane, octane, and benzene were obtained from Fluka Chemie AG (puriss p.a. > 99.5 mol %) and used without further purification. All solvents were kept over freshly activated molecular sieve type 4 A (Union Carbide) for several days before use. The purity was checked by gas−liquid chromatography analysis and was found to be higher than 99.5 mol %. Experimental values of density (ρ) of the pure liquids, along with literature values at 298.15 K, are given in Table 1.

Procedure. The binodal curves were determined by the cloud titration method, in a thermostated cell equipped with a Teflon-coated magnetic bar using an apparatus similar to that described elsewhere.[10] The thermostated temperature was controlled by a temperature controller, which maintained a constant temperature within ±0.01 K. The titrant was added in small increments from the jacketed microburet, and the contents of the cell were mixed for proper mixing and equilibrium. The amount of titrant thus added was calculated from its volume and density measured at 293.15 K with an Anton Paar digital densimeter (model DMA 60/602). The composition of the ternary mixture at the first appearance of turbidity gave one point on the binodal curve. The procedure was repeated a number of times, and a series of LLE measurements were made by changing the composition of the mixture. We estimate the accuracy of our measurements to generally be ±0.005 in mass fraction. The tie-line measurements were obtained by mixing a known weight in such proportions that they formed a heterogeneous mixture in a thermostated cell. The two-phase mixture was stirred for at least 1 h and then left to settle for at least 2 h. Once equilibrium had been reached, samples of both phases were carefully withdrawn with glass syringes and analyzed by the refractive index method as described in detail by Briggs and Comings.[11] The refractive index was measured with an accuracy of 0.0001, and the precision of this method was better than 0.001 mass fraction.

Table 1. Experimental and Literature Values of ρ of Pure-Component Liquids at 293.15 K

liquid	ρ/(g·cm^{-3}) this work	ρ/(g·cm^{-3}) literature
2-ethoxyethanol	0.925 18	0.925 206
hexane	0.654 81	0.654 846
heptane	0.679 47	0.679 427
octane	0.698 69	0.698 728
benzene	0.873 69	0.873 619
water	0.997 04	0.997 046

Table 2. Binodal Curve Composition at 293.15 K

ω_1	ω_2	ω_1	ω_2
ω_1 (2-EE + 10 Mass % Water) + ω_2 (Hexane) + ω_3 (Benzene)			
0.835	0.165	0.240	0.509
0.759	0.179	0.137	0.681
0.583	0.250	0.077	0.824
0.463	0.325	0.068	0.932
0.341	0.402		
ω_1 (2-EE + 10 Mass % Water) + ω_2 (Heptane) + ω_3 (Benzene)			
0.827	0.173	0.244	0.537
0.713	0.175	0.134	0.689
0.566	0.250	0.073	0.803
0.446	0.327	0.068	0.932
0.340	0.416		
ω_1 (2-EE + 10 Mass % Water) + ω_2 (Hexane) + ω_3 (Benzene)			
0.825	0.175	0.360	0.490
0.764	0.193	0.267	0.607
0.609	0.276	0.155	0.816
0.486	0.367	0.137	0.863

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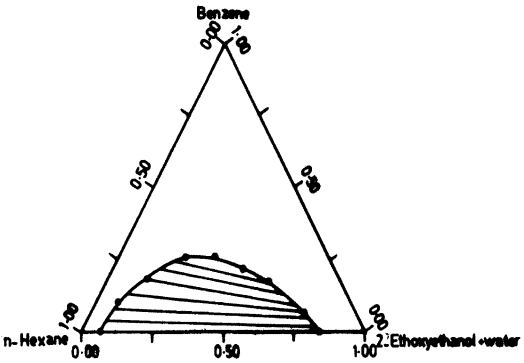

Figure 1. Binodal curve for ω_1 (2-EE + 10 mass % water) + ω_2 (hexane) + ω_3 (benzene).

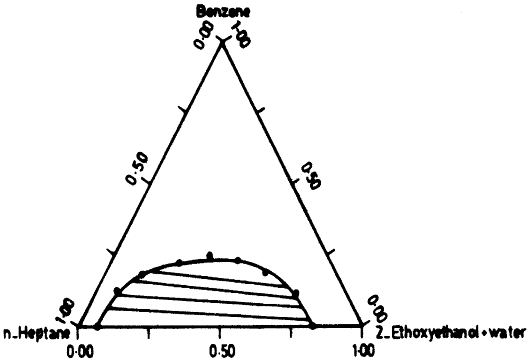

Figure 2. Binodal curve for ω_1 (2-EE + 10 mass % water) + ω_2 (heptane) + ω_3 (benzene).

Table 3. Tie-Line Data for ω_1 (2-Ethoxyethanol + 10 Mass % Water) + ω_2 (Hexane or Heptane or Octane) + ω_3 Benzene at 293.15 K

ω_1	ω_2	ω_3	ω_1	ω_2	ω_3
Solvent-Rich Phase			*n*-Hexane-Rich Phase		
0.825	0.160	0.015	0.070	0.890	0.040
0.785	0.170	0.045	0.080	0.840	0.080
0.755	0.180	0.065	0.100	0.770	0.130
0.725	0.190	0.085	0.135	0.685	0.180
0.655	0.220	0.125	0.175	0.615	0.215
0.595	0.245	0.160	0.215	0.545	0.240
Solvent-Rich Phase			*n*-Heptane-Rich Phase		
0.810	0.170	0.020	0.070	0.865	0.065
0.760	0.175	0.065	0.080	0.810	0.110
0.725	0.180	0.095	0.110	0.730	0.160
0.660	0.205	0.135	0.175	0.630	0.195
Solvent-Rich Phase			*n*-Octane-Rich Phase		
0.810	0.175	0.010	0.160	0.800	0.040
0.795	0.180	0.025	0.180	0.760	0.060
0.765	0.190	0.045	0.225	0.680	0.095

Results and Discussion

Experimental Data. Liquid−liquid equilibrium data for the three quaternary systems studied here at 293.15 K are presented in Table 2 and illustrated in Figures 1−3 for comparison. The experimental tie-line data for the systems are given in Table 3 and fit well on the binodal curves, indicating the accuracy of the experimental tie-line data. As can be seen from Figure 1, the order of the size of the two-phase region is as follows: hexane > heptane > octane.

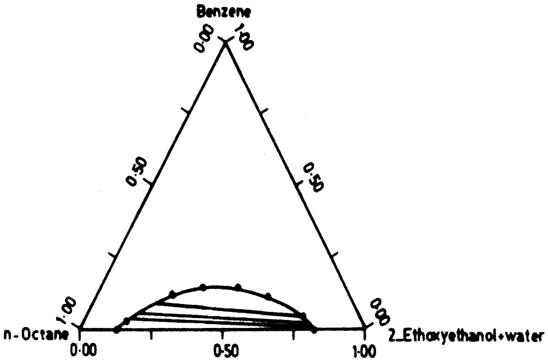

Figure 3. Binodal curve for ω_1 (2-EE + 10 mass % water) + ω_2 (octane) + ω_3 (benzene) at 293.15 K.

Data Correlation. The NRTL model was used to correlate the LLE data in the present work. The multicomponent form of the NRTL equation is given by[5]

$$G^{E} = \sum_{i=1}^{M} x_i \frac{\sum_{j=1}^{M} \tau_{ji} G_{ji} x_j}{\sum_{k=1}^{M} G_{ki} x_k} \tag{1}$$

with $\tau_{ji} = (g_{ji} - g_{ii})/(RT)$ and $G_{ij} = \exp(-\propto_{ji}\tau_{ji})$, where G^E is the molar excess Gibbs energy, g_{ij} is the energy parameter in the NRTL equation, M is the number of components, R is the gas constant, T is the absolute temperature, x_i is the mole fraction of component i, and $\propto_{ji}$ is the nonrandomness parameter which can be set to a predetermined value ranging from 0.2 to 0.5 as recommended by Renon and Prausnitz.[5] The objective function, F, was used to minimize the difference between the experimental and calculated mole fractions.

$$F = \sum_{i=1}^{n} \min \sum_{j=1}^{3} \sum_{i=1}^{2} (x_{jl}^{\text{exp}}(i) - x_{jl}^{\text{cal}}(i))^2 \tag{2}$$

where $x_{jl}^{\text{exp}}(i)$ is the experimental mole fraction, $x_{jl}^{\text{cal}}(i)$ is the calculated mole fraction, and n is the number of experimental tie-lines. The values of g_{11} could be chosen arbitrarily and fixed during the computation, and the values of the five parameters of the NRTL model g_{22}, g_{33}, g_{12}, g_{13}, and g_{23} were calculated by using the Hooke and Jeeves direct search method.[12]

The parameters calculated in this way are given in Table 4. Also included in the table is the root-mean-square deviation (RMSD):

$$\text{RMSD} = 100\left(\sum_{i=1}^{n} \min \sum_{j=1}^{3} \sum_{l}^{2} \frac{(x_{jl}^{\text{exp}}(i) - x_{jl}^{\text{cal}}(i))^2}{6M}\right)^{1/2} \tag{3}$$

where x is the mole fraction, i is the number of components, j is the number of phases, l is the number of tie-line points, n is the total number of components, and M is the total

Table 4. NRTL Parameters (g_{ij}, J·mol^{-1}) and (α_{ij}) for the Systems ω_1 (Solvent + 10 Mass % Water) + ω_2 (*n*-Alkane) + ω_3 (Toluene) at 293.15 K

system	g_{11}	g_{22}	g_{33}	g_{12}	g_{13}	g_{23}	α_{12}	α_{13}	α_{23}	RMSD
hexane	2155	9984	3544	9526	7606	8974	0.279	0.460	0.335	0.292
heptane	2155	10010	2821	9500	7926	9485	0.273	0.460	0.330	0.355
octane	2155	12000	8993	10070	6920	899.96	0.268	0.295	0.377	0.016

number of LLE sets. RMSD may be regarded as a measure of the precision of the correlation.

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