

Ternary Liquid-Liquid Equilibrium Data for the Water-Ethanol-Benzene System

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Ternary liquid-liquid equilibrium data at 30, 40, and 55 °C for the water-ethanol-benzene system are presented. The tie-line data are well correlated by the methods of Hand and Othmer-Tobias. The experimental data were also fitted with the modified UNIQUAC equation for the activity coefficients, using the isoactivity conditions as restraint equations.

Introduction

Dehydration of aqueous ethanol to high-purity alcohol for beverage and motor fuel uses is usually performed by azeotropic distillation with benzene at 1 atm (1). In the condenser, two liquid phases are formed; they are separated and the benzene-rich phase is returned to the column. Since distillation behavior is very sensitive to the composition of the reflux (2), it is necessary to predict accurately the liquid-liquid phase equilibrium in the splitter, in the temperature range 25-65 °C. For the water-ethanol-benzene system, at 20, 25, 35, 45, 55, and 64 °C liquid-liquid equilibrium data are reported (3-5). In order to cover the whole temperature range, the liquid-liquid equilibrium data for this system were measured at 30, 40, and 55 °C. This last temperature was investigated as a check on our experimental procedure.

Experimental Section

All chemicals used in this study were of reagent grade and were used directly without any further purification. Bidistilled water was used throughout the work.

Ternary liquid-liquid equilibrium data were determined by stirring different mixtures of the three components within the heterogeneous system in an equilibrium cell. This cell was equipped with a mechanical stirrer operated by a stirring motor and two windows with Teflon plugs for the withdrawal of samples for the analysis of the two layers. The equilibrium cell was coated with a jacket for the circulating fluid, thermostatically controlled by an Ultra-Thermostat Lauda within the range of 0.025 °C. The temperature in the equilibrium chamber was measured with the aid of precision Taylor thermometers within 0.05 °C after applying correction for the exposed stem.

After equilibrium was reached, an aliquot part of each layer was withdrawn with a precision Hamilton syringe and the composition of the three components was determined by gas chromatography in conjunction with calibration curves which were prepared with systems, whose composition was known, near the solubility curve at 20 °C. The apparatus used was the Carlo Erba Fractovap 2400 T gas chromatograph with Poropak (2 m) column and thermal conductivity detector. The peak areas of the chromatogram were measured with a Hewlett-Packard computing integrator S-3380. For each sample, four analyses were performed to obtain a mean value, whose accuracy was within 1%.

Results and Discussion

The experimental results are given in Table I. The tie-line data at all the temperatures are satisfactorily correlated by the method of Hand (6) and Othmer and Tobias (7). Table II gives

Table I. Liquid-Liquid Equilibrium Mole Fractions for the Water-Ethanol-Benzene System

aqueous phase			organic phase		
X_{WW}	X_{EW}	X_{BW}	X_{WB}	X_{EB}	X_{BB}
30 °C					
0.944	0.055	0.001	0.014	0.015	0.971
0.864	0.133	0.003	0.012	0.053	0.935
0.752	0.233	0.015	0.031	0.123	0.846
0.742	0.243	0.015	0.046	0.138	0.816
0.702	0.273	0.025	0.053	0.166	0.781
0.646	0.315	0.039	0.081	0.194	0.725
0.635	0.314	0.051	0.085	0.203	0.712
0.575	0.343	0.082	0.096	0.242	0.662
0.503	0.370	0.127	0.131	0.274	0.595
0.462	0.376	0.162	0.157	0.288	0.555
0.461	0.385	0.154	0.153	0.302	0.545
0.444	0.377	0.179	0.172	0.302	0.526
0.366	0.378	0.256	0.236	0.349	0.415
40 °C					
0.947	0.052	0.001	0.010	0.019	0.971
0.867	0.129	0.004	0.017	0.065	0.918
0.776	0.210	0.014	0.045	0.149	0.806
0.751	0.233	0.016	0.061	0.163	0.776
0.705	0.270	0.025	0.091	0.200	0.709
0.656	0.305	0.039	0.098	0.228	0.674
0.640	0.306	0.054	0.100	0.230	0.670
0.581	0.324	0.094	0.143	0.265	0.592
0.446	0.357	0.197	0.212	0.316	0.472
0.407	0.356	0.237	0.240	0.324	0.436
55 °C					
0.952	0.046	0.002	0.014	0.026	0.960
0.949	0.049	0.002	0.014	0.029	0.957
0.870	0.125	0.005	0.031	0.094	0.875
0.789	0.197	0.014	0.064	0.181	0.755
0.774	0.209	0.017	0.070	0.183	0.747
0.761	0.223	0.016	0.086	0.203	0.711
0.720	0.256	0.024	0.116	0.241	0.643
0.673	0.293	0.034	0.137	0.267	0.596
0.653	0.287	0.060	0.151	0.268	0.581
0.557	0.316	0.127	0.222	0.302	0.476
0.506	0.343	0.151	0.305	0.344	0.351

Table II. Linear Correlation Coefficients for the Hand and Othmer-Tobias Correlations

correlation	correlation coeff		
	30 °C	40 °C	55 °C
Hand	0.9992	0.9986	0.9987
Othmer-Tobias	0.9973	0.9949	0.9981

Table III. Estimated Values of Composition at the Plait Points

temp, °C	X_W	X_E	X_B
30	0.282	0.365	0.353
40	0.326	0.344	0.330
55	0.375	0.354	0.271

the linear correlation coefficients for the two methods and shows that the Hand correlation fits the data better than the other correlation. The correlations are shown in Figures 1 and 2. The dependence of solubility on temperature is clearly shown in these figures. Table III gives the estimated values of composition at the plait points.

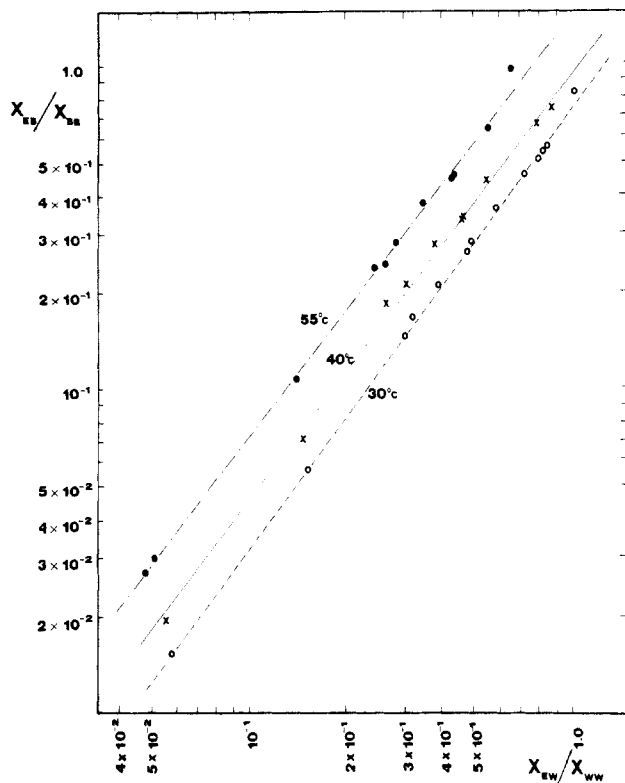


Figure 1. Hand correlation.

Table IV. Binary Parameters of the Modified UNIQUAC Equation for the Water (1)-Ethanol (2)-Benzene (3) System

$T, ^\circ\text{C}$	a_{12}, K	a_{21}, K	a_{23}, K	a_{32}, K	a_{13}, K	a_{31}, K
30	-568.9	-393.0	-239.0	-49.2	360.2	1298.3
40	-577.9	-416.6	-299.2	-39.7	365.6	1243.0
55	-247.3	-396.4	-279.9	93.7	368.0	1160.0

The experimental data were also correlated with the modified UNIQUAC equation for the activity coefficients (γ) using the isoactivity conditions as restraint equations

$$\ln \gamma_i = \ln (\phi_i/x_i) + 1 - (\phi_i/x_i) + (z/2)q_i \{ \ln (\theta_i/\phi_i) + (\phi_i/\theta_i) - 1 \} + q_i' \{ - \ln (\sum_j \theta_j' \tau_{ji}) + 1 - \sum_j (\theta_j' \tau_{ij} / \sum_k \theta_k' \tau_{kj}) \} \quad (1)$$

where

$$\phi_i = r_i x_i / \sum_j r_j x_j$$

$$\theta_i = q_i x_i / \sum_j q_j x_j$$

$$\theta_i' = q_i' x_i / \sum_j q_j' x_j$$

$$\tau_{ij} = \exp(-a_{ij}/T)$$

r , q , and q' are pure-component constants (9). In Table IV, the six binary parameters of the modified UNIQUAC equation are reported. The parameters for the partially miscible binary (water-benzene) were obtained from the binary mutual solubility data (10). The other parameters were obtained by a data-reduction method based on the maximum-likelihood principle (11). The mean average deviation between experimental and calculated values of compositions was 0.018 mole fraction. The parameters obtained in this work are not comparable with those obtained for the same system at temperatures not very far removed from our conditions and compiled in the DECHEMA series. The reason for this apparent incongruity lies in the different equations employed: in the DECHEMA compilation data reduction is performed by using the original UNIQUAC equation, while we used the modified UNIQUAC equation as

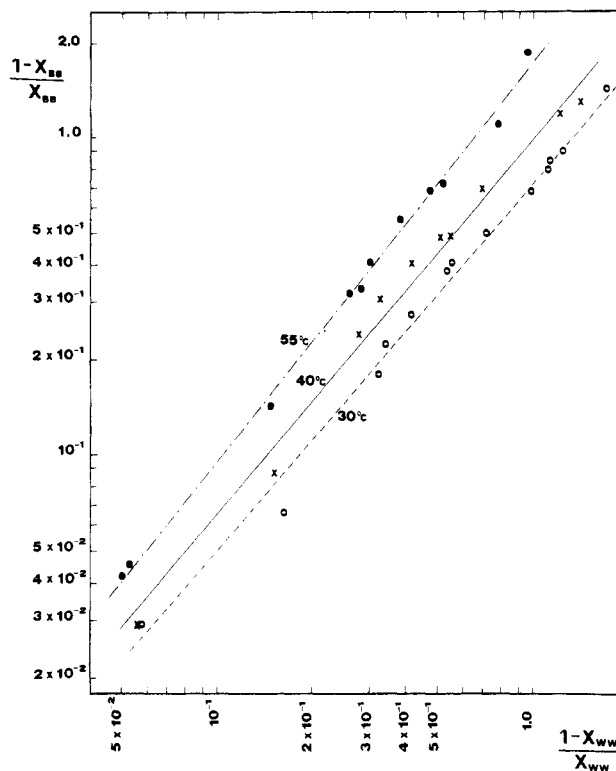


Figure 2. Othmer-Tobias correlation.

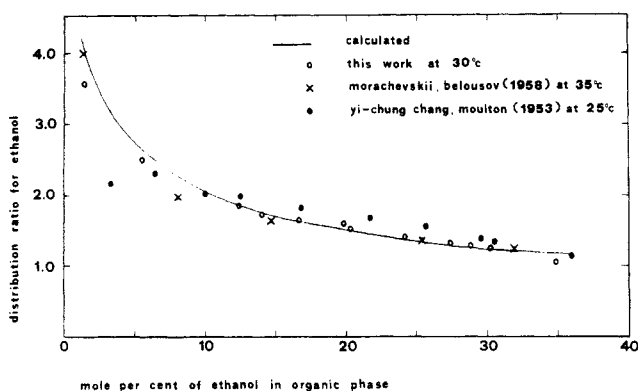


Figure 3. Distribution ratio for ethanol at 30 °C.

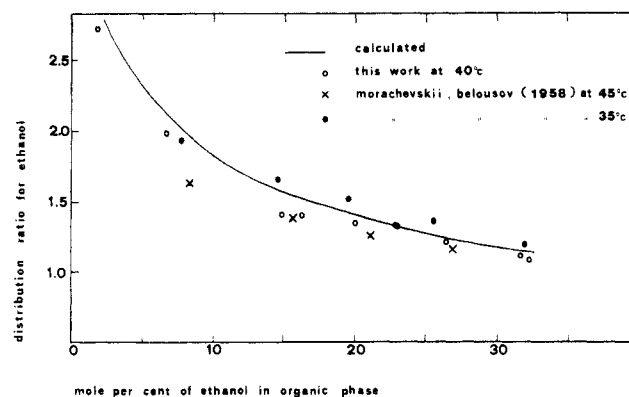


Figure 4. Distribution ratio for ethanol at 40 °C.

suggested by Anderson and Prausnitz (8) for those systems containing water or/and alcohols.

As shown in Figures 3-5, the calculated values of the distribution ratio for ethanol fall within the experimental uncertainties. However, the parameters for both miscible binaries do not have physical meaning for they predict negative devia-

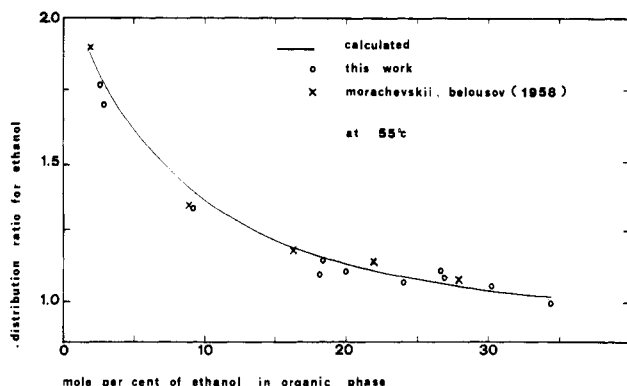


Figure 5. Distribution ratio for ethanol at 55 °C.

tions from Raoult's law. In other words, they cannot be used to predict vapor-liquid equilibrium as discussed by Yee et al. (12); they are only useful in describing liquid-liquid equilibrium. In Figure 5 our experimental values of the distribution ratio for ethanol at 55 °C are compared with those of Morachevskii and Belousov (5) at the same temperature; the two sets are in fair agreement.

Glossary

X_{EW}	liquid mole fraction of E in the W-rich phase
γ_i	activity coefficient of component i
θ_i	area fraction of component i
θ'_i	modified area fraction of component i

ϕ_i segment fraction of component i

Subscripts

B	component (benzene)
E	component (ethanol)
W	component (water)

Registry No. Benzene, 71-43-2; ethanol, 64-17-5.

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Effect of Temperature on the Apparent Molal Volume of Ethylurea in Aqueous Solutions

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The densities of aqueous solutions of ethylurea in the concentration range 0.1–8 *m* have been measured at 15, 25, 35, and 50 °C. From densities the partial molal volumes of water, \bar{V}_1 , and ethylurea, \bar{V}_2 , and the apparent molal volumes of ethylurea, Φ_V , have been calculated. The latter have been fitted to two polynomials. The first gives the dependence of Φ_V on concentration, the second on temperature. Analysis of the dependence rests on the comparison with urea. The presence of the hydrophobic moiety in ethylurea is clearly reflected in concentration as well as temperature dependence. The implications for protein denaturation by ethylurea are briefly discussed.

For interpretation of conformational changes of globular proteins in aqueous solutions brought about by a denaturant, e.g., urea, it is useful to possess knowledge of the interaction between that denaturant and water. Urea has long been known as a strong denaturant for globular proteins since, depending on concentration, it produces partial or complete unfolding of protein molecules (1). Therefore, it is understandable that a large number of studies have dealt with the thermodynamic and other relevant properties of aqueous urea solutions. The main finding has been that urea is a statistical structure breaker. For details, the reader is referred to the review by Franks (2).

Introduction of an alkyl group into the urea molecule influences its denaturing activity. However, whereas methylurea does not differ much from urea in that respect, ethylurea differs

distinctly from urea in denaturing activity (3, 4). The difference should very likely also exist in the interaction between ethylurea, as compared to urea, and water. Among the thermodynamic properties the partial molal volume is a rather sensitive measure of that interaction. Additional information is obtained by determining the temperature coefficient of the apparent molal volume. Needless to say, the volume data are also interesting per se. The apparent molal volumes of ethylurea were determined at 15, 25, 35, and 50 °C.

Experimental Section

Materials. Ethylurea (Merck, laboratory grade) was twice recrystallized from hot methanol. Before use, it was dried under vacuum over P_2O_5 at 60 °C for 24 h.

Density Measurements. The densities were measured with a precision density meter DMA-02 (Anton Paar, Graz). The temperature of the cell compartment was controlled to ± 0.01 °C with a Heto circulating thermostat. The temperature of the thermostat was set to ± 0.005 °C with a platinum resistance thermometer. The instrument was calibrated with air and water. Since all solutions must be free of large particles, before measurement solutions were filtered through Millipore filters (type HA, pore size 0.45 μm). For each ethylurea concentration at least three measurements were performed. After each series of measurements, the cell was washed and dried and the calibration constant redetermined. Under the existing experimental conditions and the time lapse for 2×10^4 periods being