Liquid−Liquid Equilibria for Water + Benzonitrile + *N,N*-Dimethylformamide, or + *N*-Methylformamide, or + Formamide

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Liquid−liquid equilibria for water + benzonitrile + formamide, water + benzonitrile + *N*-methylformamide, and water + benzonitrile + *N,N*-dimethylformamide were studied in the temperature range 25 °C−45 °C with analysis by gas chromatography. Phase diagrams, including experimentally determined tie lines and plait points for the systems including substituted formamides, are reported at each temperature. Distribution curves and enthalpy of transfer values of the amide from benzonitrile to water are given. Solubility of benzonitrile in formamide and of formamide in benzonitrile is estimated as a function of temperature.

Introduction

Benzonitrile is a compound from which new molecules with interesting chemical and biological properties have been synthesized (Caram et al., 1984; Samaniego et al., 1994; Rodríguez et al., 1995). There are few published results on the thermophysical properties of benzonitrile and its mixtures. Thus, taking into account that any potential application of the new molecules will be favored if adequate separation methods for recovering benzonitrile are available, we are involved in a continuing effort toward obtaining basic thermodynamic data of mixtures containing this solvent.

Previously, we have reported solubility data in ternary systems containing water + benzonitrile + an aliphatic alcohol (Botto et al., 1989; Grande et al., 1995; Grande et al., 1996). In this work, we report solubility data for ternary mixtures containing water + benzonitrile with formamide, *N*-methylformamide, and *N,N*-dimethylformamide.

Experimental Section

Bidistilled water and analytical grade benzonitrile (Carlo Erba, 99% purity), formamide (Merck, 99.5%), *N*-methylformamide (Aldrich, 99%), and *N,N*-dimethylformamide (Aldrich, 99.8%) were used as received. Chromatographic controls showed that in the case of benzonitrile impurity concentrations were well below 0.05%. In the case of the formamides minor concentrations of water (around 0.1% in the case of formamide, 0.1% for *N*-methylformamide, and 0.15% for *N,N*-dimethylformamide) were detected. As in our previous work, at these concentration levels of water in the formamides, calibration curves for these compounds were directly corrected by employing data from the water calibration lines.

Samples were prepared in glass tubes and placed in a thermostat controlled to ±0.1 K until equilibrium was attained. Each phase composition was analyzed by conventional gas chromatography, employing a thermal conductivity detector under different experimental conditions for the three systems.

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Table 1: Solubility Data for the System Water (A) + Benzonitrile (B) + Formamide (C) at Several Temperatures

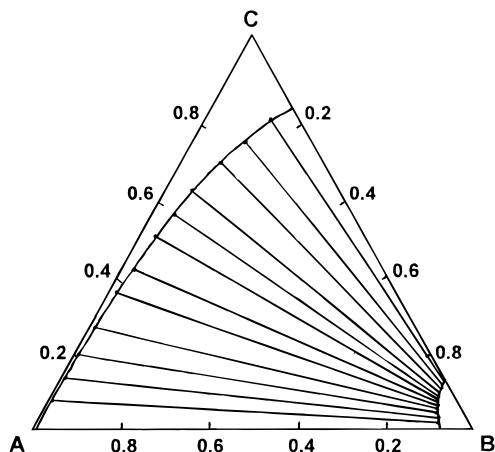| x_{AA}	x_{BA}	x_{AB}	x_{BB}	x_{AA}	x_{BA}	x_{AB}	x_{BB}
$t = 25$ °C
0.935	0.002	0.049	0.946	0.490	0.018	0.027	0.917
0.874	0.003	0.048	0.943	0.423	0.021	0.023	0.915
0.820	0.004	0.047	0.934	0.357	0.034	0.016	0.912
0.742	0.006	0.039	0.930	0.252	0.051	0.013	0.911
0.651	0.007	0.033	0.925	0.179	0.072	0.010	0.909
0.584	0.008	0.030	0.922	0.095	0.098	0.007	0.903
$t = 30$ °C
0.930	0.003	0.060	0.934	0.484	0.019	0.037	0.900
0.868	0.004	0.057	0.932	0.414	0.027	0.032	0.898
0.811	0.005	0.051	0.925	0.345	0.036	0.028	0.895
0.736	0.007	0.045	0.916	0.245	0.058	0.025	0.890
0.644	0.009	0.039	0.912	0.167	0.079	0.013	0.889
0.577	0.012	0.038	0.901	0.084	0.107	0.008	0.888
$t = 35$ °C
0.925	0.004	0.071	0.923	0.477	0.022	0.043	0.889
0.863	0.005	0.070	0.918	0.408	0.031	0.038	0.887
0.805	0.006	0.064	0.909	0.338	0.039	0.034	0.885
0.731	0.007	0.060	0.899	0.234	0.067	0.026	0.883
0.638	0.011	0.051	0.896	0.152	0.092	0.014	0.881
0.571	0.016	0.047	0.892	0.065	0.124	0.008	0.874
$t = 40$ °C
0.920	0.004	0.091	0.897	0.467	0.026	0.057	0.868
0.860	0.005	0.085	0.894	0.395	0.033	0.050	0.865
0.798	0.006	0.080	0.886	0.327	0.047	0.045	0.863
0.727	0.008	0.070	0.879	0.221	0.075	0.033	0.862
0.630	0.014	0.063	0.876	0.138	0.098	0.017	0.861
0.568	0.017	0.058	0.873	0.052	0.137	0.009	0.859
$t = 45$ °C
0.913	0.005	0.114	0.873	0.458	0.031	0.062	0.845
0.853	0.006	0.110	0.866	0.389	0.034	0.057	0.844
0.788	0.007	0.100	0.861	0.317	0.055	0.047	0.843
0.723	0.010	0.090	0.855	0.213	0.081	0.034	0.842
0.620	0.017	0.077	0.849	0.123	0.112	0.018	0.841
0.563	0.019	0.070	0.848	0.043	0.143	0.009	0.840

In the case of *N*-methylformamide, the column was filled with 10% (volume) FFAP on Chromosorb BW-HP. The initial temperature was 120 °C and was maintained for min before setting on a 10 K·min⁻¹ ramp. The temperature ramp was stopped at 170 °C and the system maintained at this value for 8 min. The carrier gas was hydrogen, flowing at 36 cm³·min⁻¹. The injector and detector temperatures were 220 °C and 200 °C, respectively.

In the case of formamide and *N,N*-dimethylformamide, the column was filled with Porapak Q. The initial tem-

Table 2: Solubility Data for the System Water (A) + Benzonitrile (B) + *N*-Methylformamide (C) at Several Temperatures[a]

x_{AA}	x_{BA}	x_{AB}	x_{BB}	x_{AA}	x_{BA}	x_{AB}	x_{BB}
			$t = 25$ °C				
0.968	0.001	0.050	0.911	0.769	0.023	0.158	0.589
0.932	0.002	0.063	0.864	0.732	0.035	0.191	0.534
0.899	0.006	0.071	0.828	0.691	0.046	0.248	0.441
0.857	0.009	0.095	0.764	0.646	0.069	0.326	0.348
0.827	0.011	0.108	0.712	0.506*	0.157*	0.506*	0.157*
0.800	0.014	0.123	0.676				
			$t = 30$ °C				
0.965	0.002	0.067	0.892	0.766	0.024	0.177	0.568
0.929	0.003	0.077	0.848	0.730	0.036	0.224	0.496
0.893	0.007	0.083	0.816	0.688	0.048	0.272	0.416
0.855	0.010	0.107	0.740	0.639	0.076	0.353	0.313
0.825	0.012	0.115	0.705	0.512*	0.160*	0.512*	0.160*
0.797	0.016	0.139	0.660				
			$t = 35$ °C				
0.963	0.002	0.075	0.879	0.792	0.019	0.176	0.595
0.925	0.006	0.088	0.834	0.757	0.028	0.200	0.536
0.891	0.008	0.095	0.792	0.722	0.040	0.267	0.439
0.853	0.011	0.126	0.713	0.676	0.059	0.322	0.362
0.819	0.017	0.139	0.679	0.518*	0.164*	0.518*	0.164*
			$t = 40$ °C				
0.953	0.003	0.095	0.857	0.782	0.024	0.179	0.589
0.920	0.008	0.101	0.816	0.746	0.039	0.233	0.500
0.884	0.014	0.112	0.771	0.705	0.055	0.283	0.421
0.843	0.016	0.145	0.683	0.653	0.080	0.348	0.335
0.815	0.020	0.153	0.648	0.525*	0.166*	0.525*	0.166*
			$t = 45$ °C				
0.948	0.007	0.120	0.829	0.780	0.025	0.221	0.526
0.912	0.010	0.125	0.789	0.745	0.039	0.266	0.457
0.879	0.017	0.136	0.722	0.699	0.059	0.330	0.370
0.839	0.018	0.173	0.636	0.635	0.093	0.450	0.225
0.812	0.021	0.192	0.584	0.535*	0.168*	0.535*	0.168*

[a] Values marked with asterisks correspond to plait points.

Table 3: Solubility Data for the System Water (A) + Benzonitrile (B) + *N,N*-Dimethylformamide (C) at Several Temperatures[a]

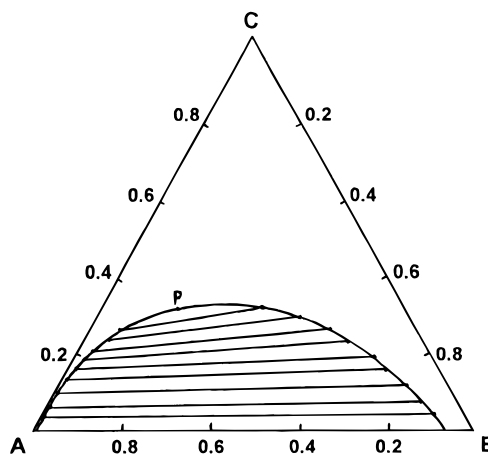| x_{AA}	x_{BA}	x_{AB}	x_{BB}	x_{AA}	x_{BA}	x_{AB}	x_{BB}
			$t = 25$ °C				
0.962	0.002	0.070	0.885	0.803	0.025	0.204	0.614
0.930	0.004	0.097	0.829	0.736	0.049	0.281	0.493
0.907	0.005	0.110	0.792	0.715	0.058	0.325	0.430
0.890	0.007	0.135	0.747	0.690	0.067	0.344	0.401
0.855	0.011	0.172	0.683	0.526*	0.190*	0.526*	0.190*
			$t = 30$ °C				
0.961	0.002	0.089	0.864	0.800	0.027	0.214	0.601
0.928	0.005	0.100	0.825	0.730	0.050	0.297	0.471
0.902	0.006	0.131	0.768	0.712	0.060	0.338	0.415
0.881	0.008	0.143	0.736	0.676	0.079	0.377	0.361
0.842	0.017	0.175	0.675	0.545*	0.177*	0.545*	0.177*
			$t = 35$ °C				
0.958	0.004	0.093	0.857	0.797	0.029	0.250	0.556
0.926	0.006	0.125	0.793	0.723	0.056	0.334	0.424
0.901	0.007	0.156	0.732	0.696	0.071	0.383	0.362
0.871	0.009	0.185	0.678	0.673	0.081	0.443	0.293
0.840	0.018	0.201	0.637	0.567*	0.161*	0.567*	0.161*
			$t = 40$ °C				
0.956	0.005	0.115	0.833	0.795	0.031	0.260	0.543
0.919	0.006	0.143	0.772	0.717	0.060	0.340	0.417
0.897	0.009	0.167	0.716	0.691	0.075	0.405	0.333
0.866	0.012	0.198	0.655	0.667	0.086	0.471	0.264
0.837	0.020	0.229	0.603	0.578*	0.156*	0.578*	0.156*
			$t = 45$ °C				
0.953	0.006	0.111	0.830	0.791	0.034	0.243	0.541
0.911	0.007	0.136	0.769	0.757	0.049	0.348	0.416
0.894	0.011	0.167	0.714	0.724	0.065	0.415	0.333
0.860	0.016	0.198	0.652	0.699	0.076	0.478	0.264
0.835	0.021	0.227	0.602	0.608*	0.140*	0.610*	0.138*

[a] Values marked with asterisks correspond to plait points.

Table 4: Solubility Values in the Binary System Benzonitrile−Formamide at Several Temperatures[a]

t/°C	x_B	x_C
25	0.136	0.097
30	0.141	0.116
35	0.151	0.126
40	0.157	0.142
45	0.162	0.160

[a] x_B is the mole fraction of benzonitrile in the formamide-rich phase; x_C is the mole fraction of formamide in the benzonitrile-rich phase.

Figure 1. Ternary phase diagram for the system water (A) + benzonitrile (B) + formamide (C) at 35 °C.

perature was 200 °C and was maintained for 1.5 min before setting on a first, 10 K·min⁻¹, ramp. The temperature ramp was stopped at 230 °C and the system maintained at this value for 2 min. The ramp was restarted and stopped when the temperature reached 240 °C and the system was maintained at this value for 10 min. The carrier gas was hydrogen, flowing at 33 cm³·min⁻¹. The injector and detector temperatures were 230 °C and 200 °C, respectively.

Under the established conditions, and as shown by calibration curves, the limit for detection of any of the involved compounds was below 10 ng. Consequently, molar fractions have an uncertainty of ±0.001.

Results and Discussion

Liquid−liquid equilibrium data obtained for the three systems in the temperature range 25 °C−45 °C are shown in Tables 1−3. In the case of *N*-methylformamide and *N,N*-dimethylformamide plait point compositions, as determined

Figure 2. Ternary phase diagram for the system water (A) + benzonitrile (B) + *N*-methylformamide (C) at 35 °C.

by the method of Hand (Treyball, 1963), are also reported. Compositions are expressed in molar fractions $x_{i,A}$ and $x_{i,B}$, where the first index refers to the component (A = water, B = benzonitrile, C = formamide, *N*-methylformamide or *N,N*-dimethylformamide) and the second to the phase (A = water-rich phase, B = benzonitrile-rich phase). The general shape of the ternary diagrams for the three systems studied can be seen in Figures 1−3 corresponding to the equilibria at 35 °C.
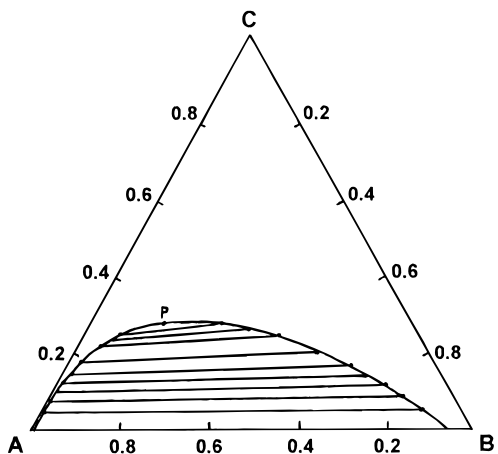
Figure 3. Ternary phase diagram for the system water + benzonitrile + *N,N*-dimethylformamide (C) at 35 °C.
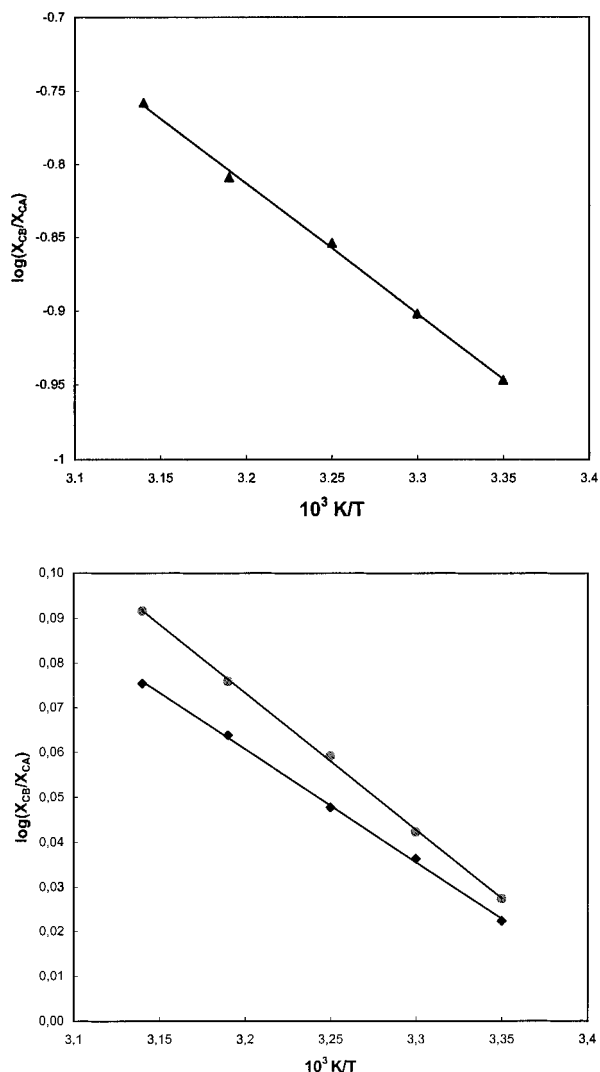

Figure 5. Logarithm of benzonitrile mole fraction in the water-rich phase as a function of formamide mole fraction at 35 °C.

Figure 6. Logarithm of formamide mole fraction in the benzonitrile-rich phase as a function of benzonitrile mole fraction at 35 °C.

slopes close to 1, indicating that no association reactions involving the formamides occur. The enthalpy of transfer of formamide from the benzonitrile-rich phase to the water-rich phase was obtained, in the three cases, taking into account that the theoretical dependence of the distribution coefficient, m_C, with temperature is given by

$$\log m_c = \Delta H_{tr}/2.3RT + K$$

The enthalpy of transfer was calculated at infinite dilution conditions in each case employing the same approach as in previous work (Grande et al., 1996). In Figure 4 the logarithm of the distribution coefficient at infinite dilution is plotted as a function of $1/T$ for each of the formamides, and transfer enthalpy values were calculated. The results were -17.2 kJ·mol^{-1} in the case of formamide, -4.8 kJ·mol^{-1} for the system containing N-methylformamide, and -6.0 kJ·mol^{-1} for N,N-dimethylformamide.

The results also enable the calculation of the compositions of coexisting phases for the binary system formamide + benzonitrile. In doing this it was observed that a linear relationship exists between log $x_{C,B}$ and $x_{B,B}$ and between log $x_{B,A}$ and $x_{C,A}$ as shown in Figures 5 and 6. Thus,

Figure 4. (a, top) Temperature dependence of the distribution coefficient at infinite dilution for the system water + benzonitrile + formamide. (b, bottom) Temperature dependence of the distribution coefficient at infinite dilution for the systems water + benzonitrile + N-methylformamide (◆) and water + benzonitrile + N,N-dimethylformamide (●).

As in the case of aliphatic alcohols, a plot of the logarithm of the amide concentration in the water-rich phase vs the logarithm of the amide concentration in the benzonitrile-rich phase shows, for the three systems, straight lines with
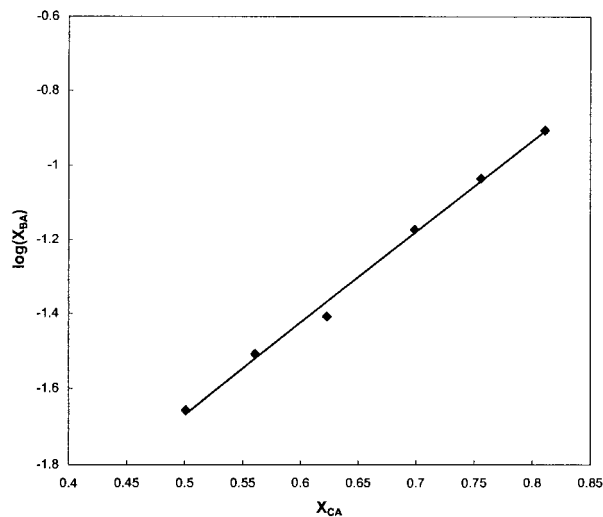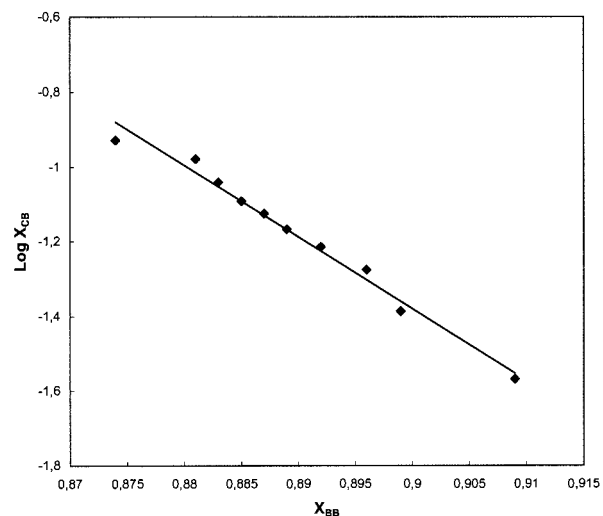
extrapolating these lines to the condition $x_{A,B} = 0$ and $x_{A,A} = 0$ respectively, composition values shown in Table 4 were obtained.

Literature Cited

Botto, G. J.; Agarás, H. H.: Marschoff, C. M. Liquid−liquid equilibrium data for the system water−benzonitrile-methanol. *J. Chem. Eng. Data* **1989**, *34*, 382−385.

Caram, J.; Martins, M. E., Marschoff, C. M.; Cafferata L. F. R.; Gros, G. E. Ritter reaction on terpenoids. I. Stereospecific preparation of (1S, 5R, 8R) and (1R, 5S, 8S) 8-acetamido-2,4,4,8-tetramethyl-3-aza-bicyclo[3.3.1]non-2-ene perchlorate. *Z. Naturforsch.* **1984,** *39b*, 972−974.

Grande, M. C.; Fresco, J.; Marschoff, C. M. Liquid−liquid equilibrium data for water + benzonitrile + ethanol or 1-propanol. *J. Chem. Eng. Data* **1995**, *40*, 1165−1167.

Grande, M. C.; Barrero, C.; Roble, M. B.; Marschoff, C. M. Liquid−liquid equilibria for water + benzonitrile + 2-propanol or 1-butanol. *J. Chem. Eng. Data* **1996**, *41*, 926−928.

Rodríguez, J. B.; Gros, E. G.; Caram, J. A.; Marschoff, C. M. Ritter reaction on terpenoids. IV. Remarkable tendency to produce 3-aza-bicyclo(3.3.1)non-2-ene systems from mono and sesquiterpenes. *Tetrahedron Lett.* **1995,** *36*, 7825−7826.

Samaniego, W. N.; Baldessari, A.; Ponce, M. A.; Rodríguez, J. B.; Gros, E. G.; Caram J. A.; Marschoff, C. M. Ritter reaction on terpenoids. III. Stereospecific preparation of (3.3.1) substituted piperidines. *Tetrahedron Lett.* **1994**, *35*, 6967−6968.

Treyball, D. E. *Liquid Extraction*; McGraw-Hill: New York, 1963; Chapter 1.