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Liquid−Liquid Equilibria for Water + Benzonitrile + 2-Propanol or 1-Butanol

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Liquid−liquid equilibria for water + benzonitrile + 2-propanol and water + benzonitrile + 1-butanol have been studied in the temperature range 25 °C−45 °C with analysis by gas chromatography. Phase diagrams, including tie lines and, for the system involving 2-propanol, plait points are reported at each temperature. Distribution curves and enthalpy of transfer values of the alcohol from water to the nitrile are given and compared with values obtained for the lower alcohols.

The need of thermodynamic data for liquid systems containing nitriles increases as new applications of these solvents are found. Benzonitrile, in particular, is an example of a compound from which new molecules with interesting biological properties have been synthesized (Caram et al., 1984; Samaniego et al., 1994). A literature search shows that few solubility measurements involving benzonitrile have been published.

Continuing our previous work (Botto et al., 1989; Grande et al., 1995), liquid−liquid equilibria in the temperature range 25 °C−45 °C for water + benzonitrile + 2-propanol and water + benzonitrile + 1-butanol are reported here.

Experimental Section

Bidistilled water, and analytical grade benzonitrile (Carlo Erba, 99% purity), 2-propanol (Mallinckrodt, 99.5% purity), and 1-butanol (Mallinckrodt, 99.5% purity) were used as received. All purity percentages are given on a mass basis. Chromatographic controls carried out on the pure components showed that, in the case of benzonitrile, impurity concentration was well below 0.5%, while in the case of the alcohols, only minor concentrations of water (around 0.1% in the case of 2-propanol and less than 0.2% for 1-butanol) were detected. At these concentration levels of water in the alcohols, calibration curves for 2-propanol and 1-butanol were directly corrected by employing data from the water calibration lines. As in our previous studies (Botto et al., 1989; Grande et al., 1995), the alcohols were not dehydrated.

Samples were prepared in glass tubes and placed in a thermostat to ±0.1 K until equilibrium was attained. Composition analysis for each phase was carried out by conventional gas chromatography, employing a thermal conductivity detector, and the experimental conditions were the same for both systems: the column was filled with Porapak Q; initial temperature was 200 °C and was maintained for 1 min before setting on a 10 $K \cdot min^{-1}$ ramp. The ramp was stopped when the oven temperature reached 230 °C and this final temperature was maintained for 15 min; carrier gas was hydrogen, flowing at 32 $cm^3 \cdot min^{-1}$. Injector and detector temperatures were 230 °C and 200 °C, respectively.

Table 1. Solubility Data for the System Water (A) + Benzonitrile (B) + 2-Propanol (C) at Several Temperatures[a]

x_{AA}	x_{BA}	x_{CA}	x_{AB}	x_{BB}	x_{CB}
t = 25 °C					
0.964	0.002	0.034	0.085	0.833	0.082
0.955	0.002	0.043	0.148	0.702	0.150
0.942	0.003	0.055	0.183	0.617	0.200
0.928	0.004	0.068	0.261	0.486	0.253
0.919	0.005	0.076	0.300	0.412	0.288
0.898	0.006	0.096	0.384	0.306	0.310
0.888	0.009	0.103	0.492	0.198	0.310
0.877	0.011	0.112	0.540	0.157	0.303
0.799*	0.026*	0.175*	0.799*	0.026*	0.175*
t = 30 °C					
0.978	0.002	0.020	0.093	0.826	0.081
0.958	0.003	0.039	0.143	0.717	0.140
0.940	0.004	0.056	0.184	0.621	0.195
0.930	0.005	0.065	0.263	0.485	0.252
0.916	0.006	0.078	0.335	0.369	0.296
0.901	0.007	0.092	0.401	0.289	0.310
0.883	0.010	0.107	0.485	0.214	0.301
0.865	0.012	0.123	0.536	0.168	0.296
0.805*	0.031*	0.164*	0.895*	0.031*	0.164*
t = 35 °C					
0.976	0.002	0.022	0.101	0.821	0.078
0.957	0.003	0.040	0.146	0.716	0.138
0.947	0.004	0.049	0.194	0.617	0.189
0.934	0.005	0.061	0.237	0.515	0.248
0.922	0.006	0.072	0.337	0.372	0.291
0.907	0.008	0.085	0.423	0.273	0.304
0.883	0.011	0.106	0.529	0.179	0.292
0.868	0.015	0.117	0.585	0.140	0.275
0.809*	0.035*	0.156*	0.809*	0.035*	0.156*
t = 40 °C					
0.978	0.003	0.019	0.125	0.799	0.076
0.960	0.004	0.036	0.178	0.689	0.133
0.950	0.005	0.045	0.192	0.631	0.177
0.938	0.006	0.056	0.233	0.534	0.233
0.929	0.007	0.064	0.325	0.402	0.273
0.912	0.009	0.079	0.448	0.261	0.291
0.891	0.012	0.097	0.544	0.181	0.275
0.872	0.015	0.113	0.632	0.125	0.243
0.815*	0.037*	0.148*	0.815*	0.037*	0.148*
t = 45 °C					
0.977	0.004	0.019	0.137	0.789	0.074
0.962	0.005	0.033	0.173	0.709	0.118
0.945	0.007	0.048	0.190	0.643	0.167
0.936	0.009	0.055	0.244	0.539	0.217
0.917	0.010	0.073	0.331	0.401	0.268
0.898	0.011	0.091	0.410	0.303	0.286
0.884	0.014	0.102	0.551	0.178	0.271
0.873	0.016	0.111	0.634	0.121	0.245
0.821*	0.038*	0.141*	0.821*	0.038*	0.141*

[a] Values marked with asterisks correspond to plait points calculated by Hand's method. x_{iA} is the mole fraction of component i in the water-rich phase; x_{iB} is the mole fraction of component i in the benzonitrile-rich phase.

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Table 2. Solubility Data for the System Water (A) + Benzonitrile (B) + 1-Butanol (C) at Several Temperatures[a]

x_{AA}	x_{BA}	x_{CA}	x_{AB}	x_{BB}	x_{CB}
		t = 25 °C			
0.994	0.000_7	0.005	0.088	0.831	0.081
0.992	0.000_6	0.007	0.141	0.695	0.164
0.991	0.000_6	0.008	0.170	0.608	0.222
0.989	0.000_6	0.010	0.214	0.496	0.290
0.987	0.000_6	0.012	0.247	0.421	0.333
0.985	0.000_5	0.014	0.283	0.351	0.366
0.983	0.000_5	0.016	0.312	0.293	0.395
0.982	0.000_4	0.018	0.345	0.223	0.432
0.981	0.000_3	0.019	0.378	0.171	0.451
0.980	0.000_3	0.020	0.426	0.095	0.479
		t = 30 °C			
0.994	0.000_7	0.005	0.093	0.829	0.078
0.993	0.000_6	0.006	0.131	0.711	0.158
0.991	0.000_6	0.008	0.147	0.659	0.194
0.990	0.000_6	0.010	0.221	0.508	0.271
0.988	0.000_5	0.011	0.258	0.412	0.330
0.986	0.000_5	0.013	0.302	0.362	0.336
0.985	0.000_5	0.015	0.328	0.272	0.400
0.983	0.000_4	0.017	0.355	0.229	0.416
0.982	0.000_3	0.018	0.395	0.162	0.443
		t = 35 °C			
0.995	0.000_6	0.004	0.111	0.785	0.104
0.993	0.000_6	0.006	0.150	0.663	0.187
0.992	0.000_5	0.007	0.201	0.542	0.257
0.990	0.000_5	0.009	0.248	0.427	0.325
0.989	0.000_5	0.011	0.293	0.356	0.351
0.987	0.000_5	0.012	0.322	0.301	0.376
0.986	0.000_4	0.014	0.333	0.271	0.396
0.985	0.000_3	0.015	0.361	0.214	0.425
0.984	0.000_3	0.016	0.394	0.151	0.455
		t = 40 °C			
0.995	0.000_5	0.004	0.107	0.816	0.077
0.994	0.000_4	0.006	0.170	0.675	0.155
0.992	0.000_4	0.008	0.187	0.599	0.214
0.991	0.000_4	0.009	0.238	0.486	0.276
0.990	0.000_3	0.010	0.275	0.402	0.323
0.989	0.000_3	0.011	0.331	0.298	0.371
0.988	0.000_3	0.012	0.343	0.265	0.392
0.987	0.000_2	0.013	0.364	0.229	0.407
0.985	0.000_2	0.015	0.405	0.162	0.433
		t = 45 °C			
0.996	0.000_4	0.004	0.146	0.768	0.086
0.995	0.000_4	0.005	0.165	0.676	0.159
0.994	0.000_3	0.006	0.217	0.558	0.225
0.992	0.000_3	0.008	0.264	0.449	0.287
0.990	0.000_3	0.010	0.281	0.401	0.318
0.989	0.000_2	0.011	0.321	0.323	0.355
0.987	0.000_2	0.013	0.331	0.279	0.389
0.986	0.000_2	0.014	0.370	0.230	0.400
0.985	0.000_2	0.015	0.394	0.168	0.462

x_{iA} is the mole fraction of component i in the water-rich phase; is the mole fraction of component i in the benzonitrile-rich phase.

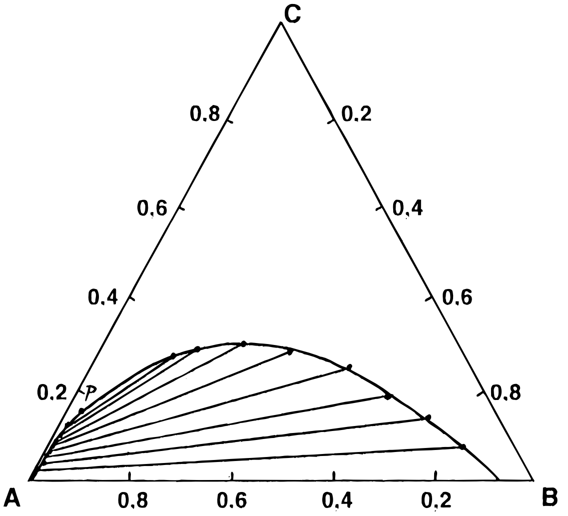

Figure 1. Ternary phase diagram for the system water + benzonitrile + 2-propanol at 35 °C.

Table 3. Transfer Enthalpies of Alcohols from Water to Benzonitrile as a Function of Alcohol Dielectric Constant

alcohol	diel const	ΔH_{tr} (kJ·mol^{-1}
methanol	32.5	−12.8
ethanol	24.3	−19.8
1-propanol	20.1	−37.2
2-propanol	17.1	−54
1-butanol	15.1	−59

Results and Discussion

Liquid−liquid equilibrium data were obtained for both systems for the temperature range 25 °C−45 °C at intervals of 5 °C, and their values are shown in Tables 1 and 2. In these tables, composition values corresponding to plait points as determined by Hand's method are also included in the case of 2-propanol. For 1-butanol, plait points do not exist. Compositions are always expressed in molar fractions $x_{i,A}$ or $x_{i,B}$ where the first index refers to the component and the second to the phase (A = water-rich phase; B = benzonitrile-rich phase). In Figure 1, the ternary diagram for the case of 2-propanol is shown only at 35 °C, since the general behavior of this system with temperature is quite similar to that of the alcohols previously studied. In Figure 2, phase diagrams are shown for the 1-butanol system at three of the five temperatures because these curves strongly differ from those of lower alcohols.

Log−log distribution curves for both systems showed straight lines with slopes close to 1 which indicates that, as in the cases of methanol, ethanol, and 1-propanol, no association occurs. Finally, since the theoretical dependence of the distribution coefficient, m_C, with temperature is given by

$$\log m_C = [(H_{C,A} - H_{C,B})/2.3RT] + K$$

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

where $H_{C,A}$ and $H_{C,B}$ are, respectively, the partial molar enthalpies of the alcohol in water and benzonitrile solutions and ΔH_{tr} is the enthalpy of transfer of the alcohol from the benzonitrile-rich phase to the water-rich phase; plotting log m_C *vs* $1/T$ allows us to obtain this value. In order to calculate the enthalpy of transfer at infinite dilution, the molar fractions of the alcohol in the water-rich phase were plotted as a function of the molar fractions in the benzonitrile-rich phase and the resulting points fitted to a fourth degree polynomial, whose slope at the origin gives the distribution coefficient at infinite dilution. In Figures 3 and 4 the logarithm of the distribution coefficient at infinite dilution is plotted as a function of $1/T$, and therefrom, enthalpies of transfer are obtained. The values found are −54 kJ·mol^{-1} for 2-propanol and −59 kJ·mol^{-1} for 1-butanol. When these transfer enthalpies are compared with those corresponding to methanol, ethanol, and 1-propanol at infinite dilution determined in the same way in previous work (Botto et al., 1989; Grande et al., 1995), it is seen that, as Table 3 shows, the exothermicity of alcohol transfer from water to benzonitrile increases as the dielectric

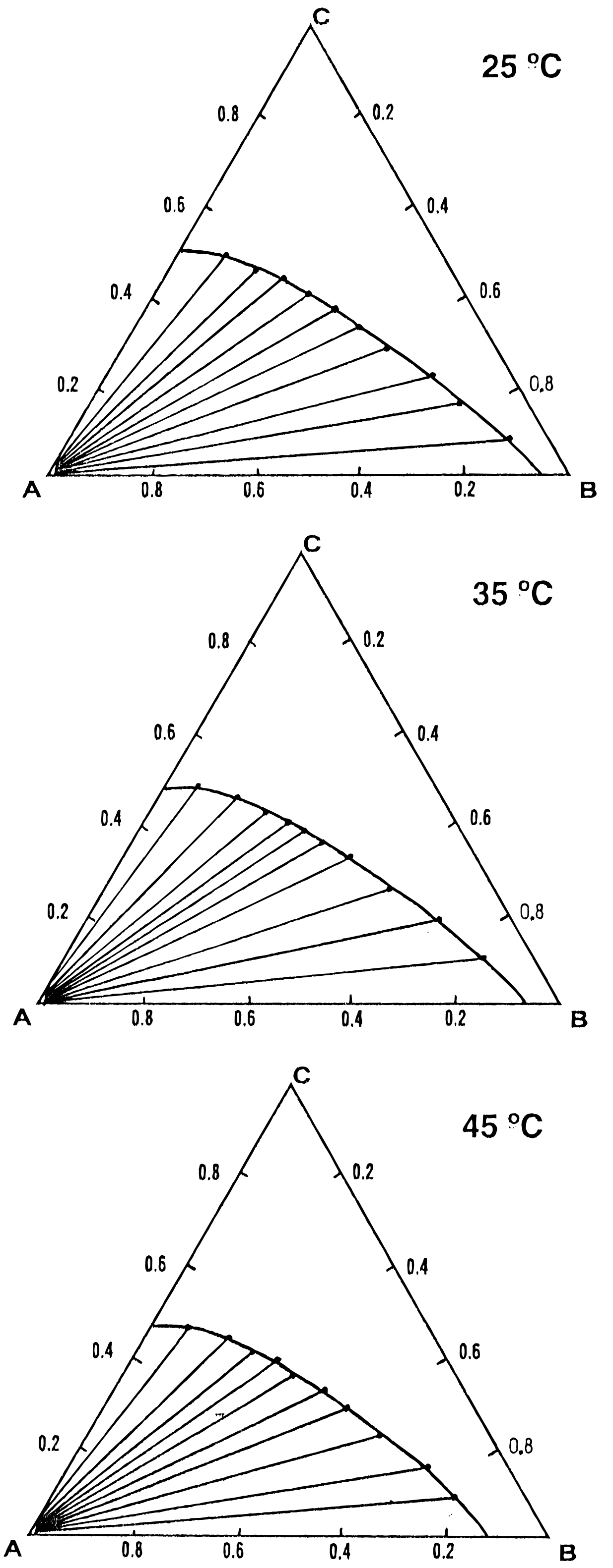

Figure 2. Ternary phase diagrams for the system water + benzonitrile + 1-butanol at several temperatures.

constant of the alcohol diminishes. Further work is under progress in order to better understand this behavior.

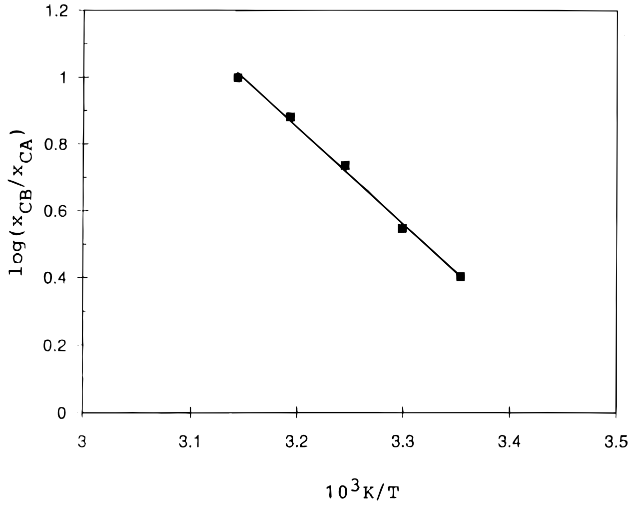

Figure 3. Temperature dependence of the distribution coefficient at infinite dilution for the system water + benzonitrile + 2-propanol.

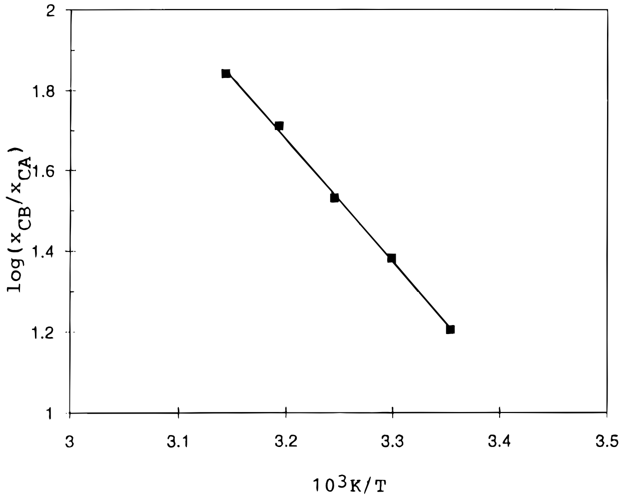

Figure 4. Temperature dependence of the distribution coefficient at infinite dilution for the system water + benzonitrile + 1-butanol.

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