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Liquid−Liquid Equilibria of Water + Benzonitrile + Propanone, or + Dimethylsulfoxide

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Liquid−liquid equilibria for the ternary systems water + benzonitrile + propanone and water + benzonitrile + dimethyl sulfoxide were studied in the temperature range (25 to 45) °C. Composition analyses of each phase were carried out by gas chromatography. Phase diagrams, including tie lines and plait points, are reported. Distribution curves are shown, and enthalpies of transfer of acetonitrile and propionitrile from water to benzonitrile were calculated.

The interest in determining thermodynamic properties of mixtures containing water and benzonitrile stems out from the fact that iminium salts with unusual properties are obtained from the reaction of benzonitrile with terpenes[1−4] and, consequently, it is important to have basic data in order to design processing equipment. Continuing our systematic work on phase equilibria in ternary mixtures containing water, benzonitrile, and a third component,[5−9] solubility data for the systems water + benzonitrile + propanone and water + benzonitrile + dimethyl sulfoxide in the temperature range (25 to 45) °C were measured and are reported in this paper.

Experimental Section

Bidistilled water and analytical grade benzonitrile (Carlo Erba, 99% purity), propanone (Sigma, 99.9% purity), and dimethyl sulfoxide (Baker, 99.9% purity) were employed as received. Chromatographic analyses showed that impurities in the three solvents were below 0.05%, respectively. Water was not detected in the chromatograms, and hence, calibration curves were not corrected.

Weighed samples were prepared in glass tubes and placed in a thermostat controlled to ±0.1 K, and phase compositions were analyzed at 2 h intervals until equilibrium was attained. Chromatographic measurements for both systems were carried out with a column filled with Chromosorb W-HP and 10% FFAP. A thermal conductivity detector was employed. In all experiments the initial temperature was fixed at 90 °C and held for 1 min; at that time a linear temperature gradient of 35 °C·min^{-1} was applied during 2 min and then the temperature was held at 160 °C until the end of the experiment. The carrier gas was hydrogen, flowing at 33 cm^3·min^{-1}, and the injection and detector temperatures were 220 °C and 200 °C, respectively. Calibration curves showed that the detection limit was below 10 ng. Hence, the molar fractions have an uncertainty of ±0.001.

Results and Discussion

Liquid−liquid equilibrium data obtained for the two systems in the temperature range (25 to 45) °C are shown in Tables 1 and 2. In the case of the mixture containing acetonitrile, plait point compositions, as determined by the

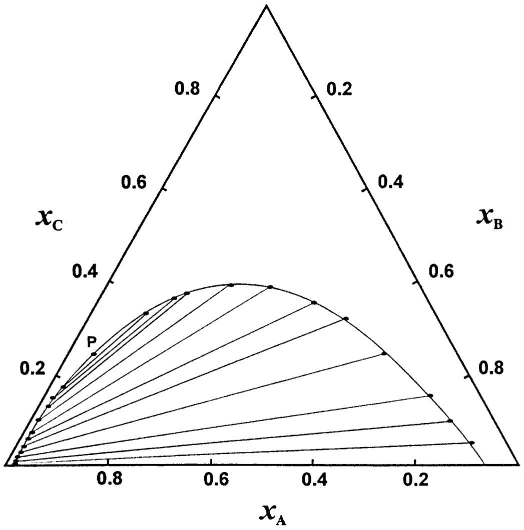

Figure 1. Ternary phase diagram for the system water (A) + benzonitrile (B) + propanone (C) at 35 °C.

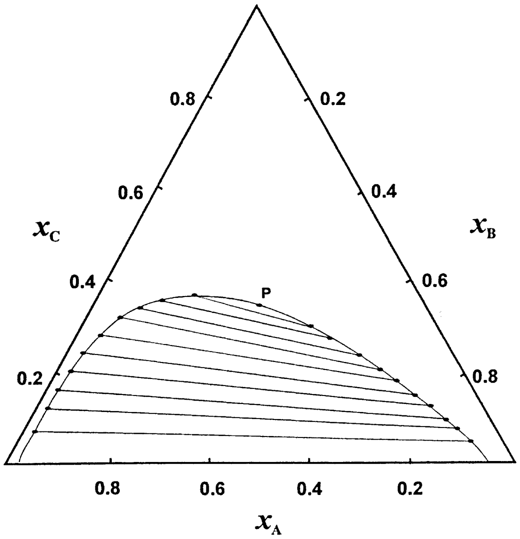

Figure 2. Ternary phase diagram for the system water (A) + benzonitrile (B) + DMSO (C) at 35 °C.

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Table 1: Solubility Data for the Ternary System Water (A) + Benzonitrile (B) + Propanone (C) at Different Temperatures[a]

x_{AA}	x_{BA}	x_{CA}	x_{AB}	x_{BB}	x_{CB}
T = 25 °C					
0.987	0.001	0.012	0.042	0.910	0.048
0.980	0.001	0.019	0.053	0.836	0.111
0.969	0.002	0.029	0.075	0.760	0.165
0.948	0.002	0.050	0.098	0.647	0.255
0.926	0.003	0.071	0.139	0.522	0.339
0.907	0.004	0.089	0.170	0.448	0.382
0.866	0.005	0.129	0.272	0.312	0.416
0.832	0.008	0.160	0.356	0.228	0.416
0.796	0.013	0.191	0.413	0.180	0.407
0.784	0.017	0.199	0.429	0.167	0.404
0.766	0.018	0.216	0.463	0.143	0.394
0.636*	0.057*	0.307*	0.636*	0.057*	0.307*
T = 30 °C					
0.992	0.001	0.007	0.052	0.899	0.049
0.984	0.001	0.015	0.070	0.808	0.122
0.978	0.002	0.020	0.076	0.774	0.150
0.963	0.003	0.034	0.108	0.641	0.251
0.947	0.003	0.050	0.159	0.509	0.332
0.931	0.004	0.065	0.190	0.438	0.372
0.916	0.006	0.078	0.235	0.367	0.398
0.891	0.009	0.100	0.303	0.282	0.415
0.846	0.013	0.141	0.436	0.165	0.399
0.823	0.017	0.160	0.469	0.147	0.384
0.801	0.021	0.178	0.500	0.127	0.373
0.684*	0.051*	0.265*	0.684*	0.051*	0.265*
T = 35 °C					
0.993	0.001	0.006	0.058	0.895	0.047
0.987	0.001	0.012	0.082	0.823	0.095
0.979	0.002	0.019	0.095	0.757	0.148
0.964	0.003	0.033	0.133	0.620	0.247
0.948	0.004	0.048	0.172	0.502	0.326
0.935	0.004	0.061	0.216	0.429	0.355
0.919	0.006	0.075	0.291	0.319	0.390
0.892	0.009	0.099	0.371	0.237	0.392
0.850	0.014	0.136	0.465	0.157	0.378
0.826	0.018	0.156	0.496	0.139	0.365
0.797	0.026	0.177	0.576	0.101	0.323
0.710*	0.047*	0.243*	0.710*	0.047*	0.243*
T = 40 °C					
0.995	0.001	0.004	0.095	0.844	0.061
0.987	0.002	0.011	0.100	0.795	0.105
0.980	0.002	0.018	0.115	0.719	0.166
0.971	0.003	0.026	0.147	0.598	0.255
0.951	0.004	0.045	0.192	0.483	0.325
0.934	0.005	0.061	0.231	0.408	0.361
0.919	0.007	0.074	0.311	0.299	0.390
0.891	0.010	0.099	0.375	0.230	0.395
0.849	0.017	0.134	0.499	0.140	0.361
0.819	0.026	0.155	0.579	0.099	0.322
0.743*	0.042*	0.215*	0.743*	0.042*	0.215*
T = 45 °C					
0.995	0.002	0.003	0.108	0.827	0.065
0.988	0.002	0.010	0.113	0.780	0.107
0.982	0.003	0.015	0.125	0.704	0.171
0.974	0.003	0.023	0.155	0.599	0.246
0.963	0.004	0.033	0.192	0.513	0.295
0.949	0.004	0.047	0.251	0.405	0.344
0.931	0.007	0.062	0.336	0.289	0.375
0.908	0.011	0.081	0.395	0.225	0.380
0.882	0.017	0.101	0.500	0.144	0.356
0.852	0.027	0.121	0.631	0.083	0.286
0.768*	0.036*	0.196*	0.768*	0.036*	0.196*

[a] Asterisks correspond to plait points.

Table 2: Solubility Data for the Ternary System Water (A) + Benzonitrile (B) + DMSO (C) at Different Temperatures[a]

x_{AA}	x_{BA}	x_{CA}	x_{AB}	x_{BB}	x_{CB}
T = 25 °C					
0.929	0.005	0.066	0.055	0.917	0.028
0.881	0.007	0.112	0.068	0.885	0.047
0.839	0.008	0.153	0.082	0.844	0.074
0.798	0.009	0.193	0.092	0.797	0.111
0.753	0.015	0.232	0.101	0.769	0.130
0.707	0.021	0.272	0.118	0.717	0.165
0.662	0.037	0.301	0.137	0.676	0.187
0.621	0.045	0.334	0.157	0.621	0.222
0.576	0.068	0.356	0.175	0.565	0.260
0.541	0.085	0.374	0.199	0.512	0.289
0.322*	0.307*	0.371*	0.322*	0.307*	0.371*
T = 30 °C					
0.925	0.006	0.069	0.064	0.907	0.029
0.867	0.008	0.125	0.082	0.861	0.057
0.820	0.010	0.170	0.093	0.824	0.083
0.789	0.012	0.199	0.113	0.776	0.111
0.739	0.016	0.245	0.128	0.731	0.141
0.696	0.027	0.277	0.137	0.691	0.172
0.634	0.049	0.317	0.155	0.653	0.192
0.596	0.062	0.342	0.178	0.596	0.226
0.549	0.094	0.357	0.195	0.541	0.264
0.497	0.128	0.375	0.233	0.470	0.297
0.328*	0.312*	0.360*	0.328*	0.312*	0.360*
T = 35 °C					
0.918	0.007	0.075	0.081	0.887	0.032
0.866	0.008	0.126	0.088	0.849	0.063
0.817	0.011	0.172	0.101	0.813	0.086
0.778	0.015	0.207	0.119	0.768	0.113
0.731	0.017	0.252	0.137	0.717	0.146
0.691	0.031	0.278	0.157	0.667	0.176
0.620	0.055	0.325	0.180	0.620	0.200
0.569	0.088	0.343	0.201	0.564	0.235
0.518	0.122	0.360	0.237	0.489	0.274
0.448	0.176	0.376	0.263	0.437	0.300
0.335*	0.316*	0.349*	0.335*	0.316*	0.349*
T = 40 °C					
0.902	0.007	0.091	0.100	0.853	0.047
0.852	0.009	0.139	0.116	0.809	0.075
0.805	0.012	0.183	0.124	0.779	0.097
0.752	0.019	0.229	0.138	0.740	0.122
0.713	0.025	0.262	0.155	0.693	0.152
0.661	0.043	0.296	0.176	0.643	0.181
0.584	0.084	0.332	0.190	0.608	0.202
0.531	0.125	0.344	0.225	0.532	0.243
0.451	0.186	0.363	0.279	0.426	0.295
0.343*	0.320*	0.337*	0.343*	0.320*	0.337*
T = 45 °C					
0.901	0.008	0.091	0.132	0.832	0.036
0.846	0.010	0.144	0.138	0.791	0.071
0.793	0.019	0.188	0.151	0.759	0.090
0.742	0.026	0.232	0.169	0.719	0.112
0.691	0.043	0.266	0.181	0.674	0.145
0.639	0.060	0.301	0.204	0.613	0.183
0.553	0.112	0.335	0.234	0.559	0.207
0.492	0.162	0.346	0.273	0.472	0.255
0.368*	0.325*	0.307*	0.368*	0.325*	0.307*

[a] Asterisks correspond to plait points.

method of Hand,[10] were calculated and 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 = propanone or DMSO) and the second to the phase (A = water-rich phase, B = benzonitrile-rich phase). The general shape of the ternary diagrams for both systems can be seen in Figures 1 and 2, which correspond to equilibria at 35 °C.

As in the case of the previously studied systems, a plot of the logarithm of propanone and DMSO concentration in the water-rich phase versus the logarithm of the concentration in the benzonitrile-rich phase shows straight lines with slopes close to 1 for both systems, which indicates that association phenomena involving these compounds are not significant.

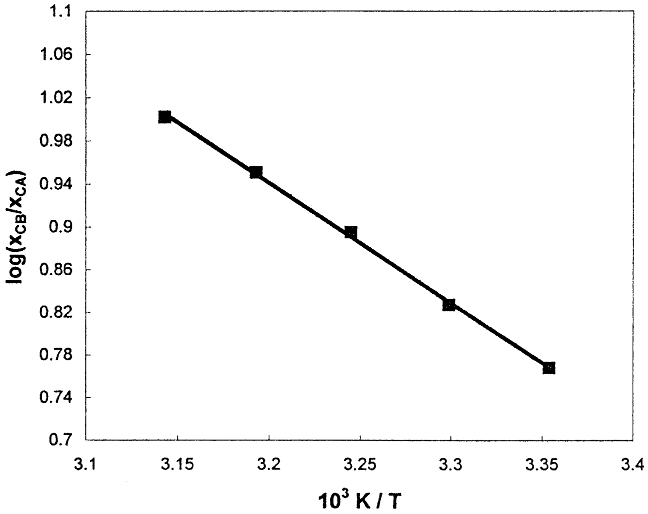

Figure 3. Temperature dependence of the distribution coefficient at infinite dilution for the system water (A) + benzonitrile (B) + propanone (C).

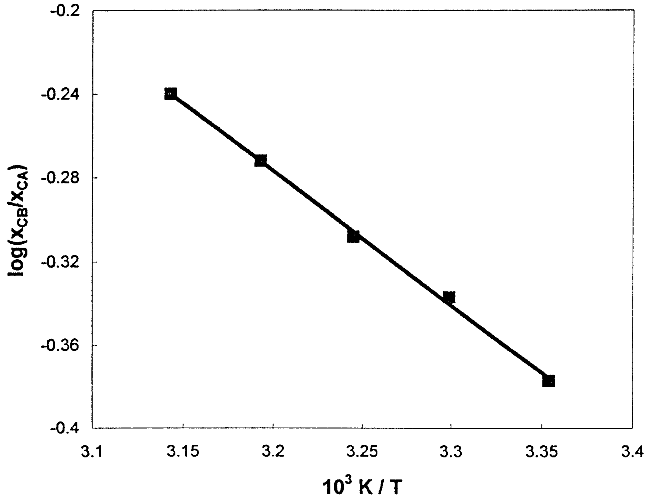

Figure 4. Temperature dependence of the distribution coefficient at infinite dilution for the system water (A) + benzonitrile (B) + DMSO (C).

The enthalpy of transfer of propanone and DMSO from the benzonitrile-rich phase to the water-rich phase was obtained in both cases by applying the equation

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

where the distribution coefficient m_C is defined as x_{CB}/x_{CA} and K is an integration constant.

In Figures 3 and 4 m_C values extrapolated at infinite dilution are plotted as a function of T^{-1}, and the resulting values for enthalpy of transfer are -21.4 kJ·mol^{-1} for the case of propanone and -12.2 kJ·mol^{-1} for DMSO.

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