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Liquid−Liquid Equilibria of Water + Benzonitrile + Acetonitrile or + Propionitrile

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Liquid−liquid equilibria for the ternary systems water + benzonitrile + acetonitrile and water + benzonitrile + propionitrile 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, for the system containing acetonitrile, plait points are reported. Distribution curves are shown and enthalpies of transfer of acetonitrile and propionitrile from benzonitrile to water were calculated. Mutual solubilities for the binary system water + propionitrile were measured in the temperature range (25 to 80)°C

Considering the promising properties of iminium salts obtained from the reaction of benzonitrile with terpenes (Caram et al., 1984; Samaniego et al., 1994; Rodríguez et al. 1995) our laboratory is involved in a systematic study of phase equilibria in ternary mixtures containing water, benzonitrile, and a third component. In previous work (Botto et al., 1989; Grande et al., 1995; Grande et al., 1996; Grande and Marschoff, 1998) solubility data for ternary systems in which the third component is an aliphatic alcohol, or a formamide were obtained. In this paper we report the obtained results for the systems water + benzonitrile + acetonitrile and water + benzonitrile + propionitrile in the temperature range (25 to 45)°C and for the binary system water + propionitrile in the temperature range (25 to 80)°C.

Experimental Section

Bidistilled water and analytical grade benzonitrile (Carlo Erba, 99% purity); acetonitrile (Aldrich, 99% purity) and propionitrile (Aldrich, 99% purity) were employed as received. Chromatographic analyses showed that impurities in benzonitrile and propionitrile were below 0.05% and 0.1% respectively. In the case of acetonitrile, minor concentrations of water (below 0.1%) were detected. At these concentration levels of water, calibration curves for the nitriles were directly corrected employing data from the water calibration lines. Thus, as in our previous work, the solvents were not dehydrated.

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 15% Carbowax. A thermal conductivity detector was employed. In all experiments the initial temperature was fixed at 70 °C and held for 6 min; at that time a linear temperature gradient of 16.25 °C min^{-1} was applied during 8 min and then the temperature was held at 200 °C until the end of the experiment. The carrier gas was hydrogen, flowing at 35 cm^3 min^{-1} and injection and detector temperatures were 230 °C and 210 °C, respectively. Calibration curves showed that the detection limit was below 10 ng. Hence, molar fractions have an uncertainty of ±0.001.

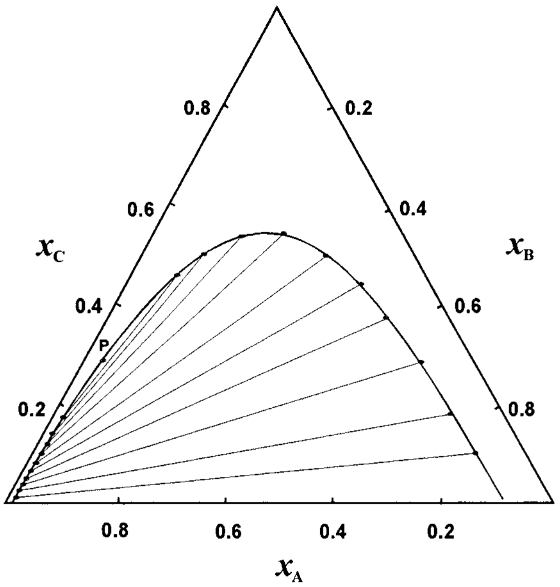

Figure 1. Ternary phase diagram for the system water (A) + benzonitrile (B) + acetonitrile (C) at 35 °C. P indicates the position of the plait point.

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 points compositions, as determined by the method of Hand (Treyball, 1963), 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 = acetonitrile, or propionitrile) and the second to the phase (A = water-rich phase, B = benzonitrile-rich phase). The general shape

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Table 1. Solubility Data for the Ternary System Water + Benzonitrile + Acetonitrile at Different Temperatures (Asterisks correspond to plait points)

x_{AA}	x_{BA}	x_{CA}	x_{AB}	x_{BB}	x_{CB}
$t = 25$ °C					
0.987	0.002	0.011	0.051	0.858	0.091
0.979	0.002	0.019	0.058	0.781	0.161
0.956	0.003	0.041	0.083	0.629	0.288
0.941	0.004	0.055	0.097	0.536	0.367
0.934	0.005	0.062	0.124	0.451	0.425
0.925	0.005	0.070	0.135	0.398	0.467
0.906	0.006	0.088	0.196	0.258	0.546
0.889	0.006	0.105	0.240	0.190	0.570
0.852	0.006	0.142	0.332	0.110	0.558
0.834	0.007	0.159	0.398	0.072	0.530
0.691*	0.012*	0.297*	0.691*	0.012*	0.297*
$t = 30$ °C					
0.986	0.002	0.012	0.060	0.849	0.091
0.972	0.003	0.025	0.066	0.786	0.148
0.948	0.009	0.043	0.082	0.658	0.260
0.943	0.005	0.052	0.103	0.574	0.323
0.937	0.005	0.058	0.116	0.492	0.392
0.928	0.005	0.067	0.137	0.417	0.446
0.916	0.006	0.078	0.180	0.307	0.513
0.884	0.006	0.110	0.248	0.195	0.557
0.843	0.007	0.150	0.314	0.135	0.551
0.807	0.007	0.186	0.383	0.089	0.528
0.695*	0.016*	0.289*	0.695*	0.016*	0.289*
$t = 35$ °C					
0.987	0.003	0.010	0.075	0.829	0.096
0.976	0.003	0.021	0.087	0.747	0.166
0.959	0.004	0.037	0.098	0.624	0.278
0.941	0.005	0.054	0.123	0.508	0.369
0.927	0.005	0.068	0.136	0.428	0.436
0.912	0.006	0.082	0.179	0.324	0.498
0.902	0.007	0.091	0.231	0.223	0.546
0.874	0.007	0.119	0.309	0.147	0.544
0.849	0.007	0.144	0.401	0.099	0.501
0.824	0.007	0.168	0.492	0.060	0.448
0.698*	0.021*	0.281*	0.698*	0.021*	0.281*
$t = 40$ °C					
0.978	0.003	0.010	0.075	0.829	0.096
0.952	0.003	0.021	0.087	0.747	0.166
0.937	0.004	0.037	0.098	0.624	0.278
0.920	0.005	0.054	0.123	0.508	0.369
0.907	0.005	0.068	0.136	0.428	0.436
0.893	0.006	0.082	0.179	0.324	0.498
0.878	0.007	0.091	0.231	0.223	0.546
0.855	0.007	0.119	0.309	0.147	0.544
0.834	0.007	0.144	0.401	0.099	0.501
0.702*	0.026*	0.272*	0.702*	0.026*	0.272*
$t = 45$ °C					
0.976	0.003	0.021	0.136	0.747	0.117
0.960	0.004	0.036	0.166	0.619	0.215
0.951	0.005	0.044	0.187	0.523	0.290
0.940	0.005	0.055	0.213	0.451	0.336
0.915	0.006	0.079	0.240	0.348	0.413
0.900	0.007	0.093	0.288	0.272	0.440
0.878	0.007	0.115	0.338	0.203	0.459
0.855	0.008	0.137	0.435	0.127	0.438
0.803	0.008	0.189	0.590	0.060	0.350
0.706*	0.031*	0.263*	0.706*	0.031*	0.263*

Table 2. Solubility Data for the Ternary System Water + Benzonitrile + Propionitrile at Different Temperatures

x_{AA}	x_{BA}	x_{CA}	x_{AB}	x_{BB}	x_{CB}
$t = 25$ °C					
0.991	0.007	0.002	0.045	0.889	0.066
0.990	0.006	0.004	0.058	0.786	0.157
0.987	0.006	0.007	0.061	0.700	0.239
0.984	0.005	0.011	0.070	0.610	0.320
0.981	0.005	0.014	0.074	0.521	0.405
0.979	0.004	0.017	0.078	0.435	0.487
0.976	0.003	0.021	0.088	0.353	0.559
0.974	0.002	0.024	0.096	0.264	0.640
0.971	0.002	0.027	0.103	0.190	0.707
0.969	0.001	0.030	0.127	0.093	0.780
$t = 30$ °C					
0.989	0.008	0.003	0.058	0.861	0.081
0.988	0.007	0.005	0.066	0.766	0.168
0.985	0.007	0.008	0.068	0.683	0.249
0.982	0.006	0.012	0.077	0.595	0.328
0.979	0.006	0.015	0.083	0.509	0.408
0.978	0.004	0.018	0.086	0.428	0.486
0.975	0.004	0.021	0.089	0.344	0.567
0.972	0.003	0.025	0.101	0.256	0.643
0.969	0.002	0.029	0.120	0.171	0.709
0.966	0.001	0.033	0.133	0.088	0.779
$t = 35$ °C					
0.987	0.009	0.004	0.069	0.844	0.088
0.984	0.009	0.007	0.078	0.753	0.169
0.983	0.007	0.010	0.080	0.669	0.251
0.979	0.007	0.014	0.091	0.579	0.330
0.977	0.006	0.017	0.094	0.494	0.412
0.975	0.005	0.020	0.097	0.410	0.493
0.972	0.004	0.024	0.105	0.326	0.569
0.970	0.003	0.027	0.108	0.247	0.645
0.966	0.003	0.031	0.128	0.161	0.711
0.964	0.002	0.034	0.147	0.078	0.775
$t = 40$ °C					
0.984	0.010	0.006	0.091	0.811	0.098
0.982	0.009	0.009	0.098	0.727	0.176
0.980	0.008	0.012	0.100	0.643	0.257
0.977	0.007	0.016	0.102	0.565	0.334
0.975	0.006	0.019	0.104	0.478	0.418
0.973	0.005	0.022	0.113	0.392	0.495
0.970	0.004	0.026	0.118	0.311	0.571
0.968	0.003	0.029	0.139	0.223	0.638
0.964	0.003	0.033	0.157	0.142	0.701
0.963	0.002	0.035	0.173	0.064	0.763
$t = 45$ °C					
0.982	0.011	0.007	0.119	0.777	0.104
0.979	0.010	0.011	0.121	0.694	0.185
0.975	0.008	0.016	0.123	0.614	0.263
0.973	0.008	0.019	0.125	0.539	0.336
0.969	0.007	0.023	0.127	0.453	0.420
0.966	0.005	0.027	0.129	0.373	0.498
0.964	0.005	0.031	0.134	0.294	0.572
0.963	0.004	0.035	0.160	0.206	0.634
0.962	0.003	0.035	0.179	0.127	0.694
0.961	0.002	0.037	0.206	0.059	0.735

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 aliphatic alcohols and formamides, a plot of the logarithm of acetonitrile and propionitrile concentration in the water-rich phase vs the logarithm of the concentration in the benzonitrile-rich phase shows straight lines with slopes close to 1 for both systems, which indicate that association phenomena involving the nitriles are not significant.

Since no specific data for mutual solubilities in the binary system water + propionitrile were found, we also carried out solubility measurements on this system in the temperature range (25 to 80)°C with the same experimental technique. The obtained data are reported in Table 3.

The enthalpy of transfer of acetonitrile and propionitrile from the benzonitrile-rich phase to the water-rich phase

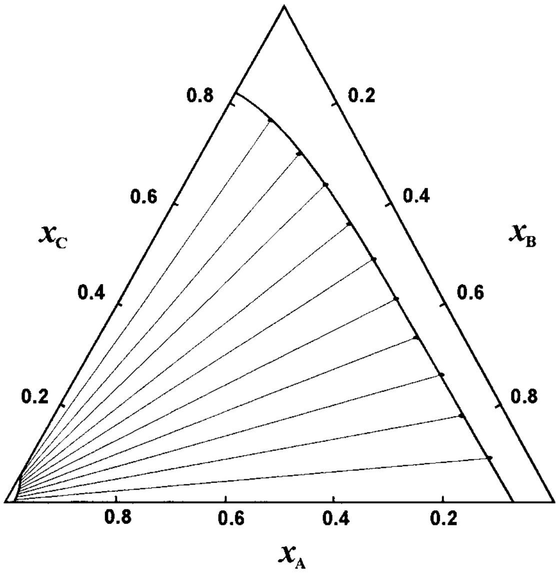

Figure 2. Ternary phase diagram for the system water (A) + benzonitrile (B) + propionitrile (C) at 35 °C.

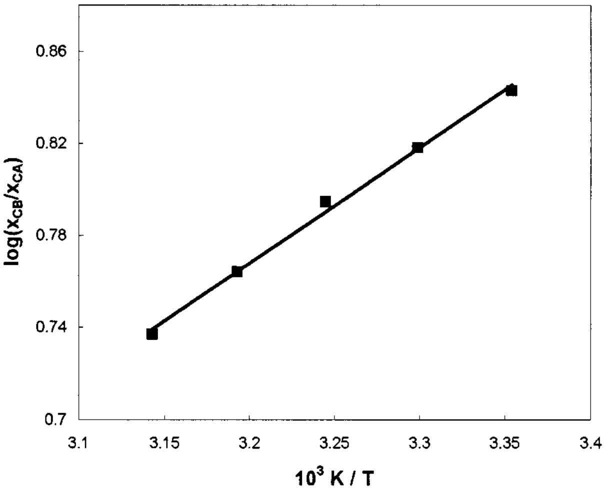

Figure 3. Temperature dependence of the distribution coefficient at infinite dilution for the system water + benzonitrile + acetonitrile

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 10.1 kJ mol^{-1} for the case of acetonitrile and 25.4 kJ mol^{-1} for propionitrile. It is to be noted that these nitriles show an endothermic enthalpy of transfer while aliphatic alcohols and formamides undergo an exothermic process when transferred from benzonitrile to water.

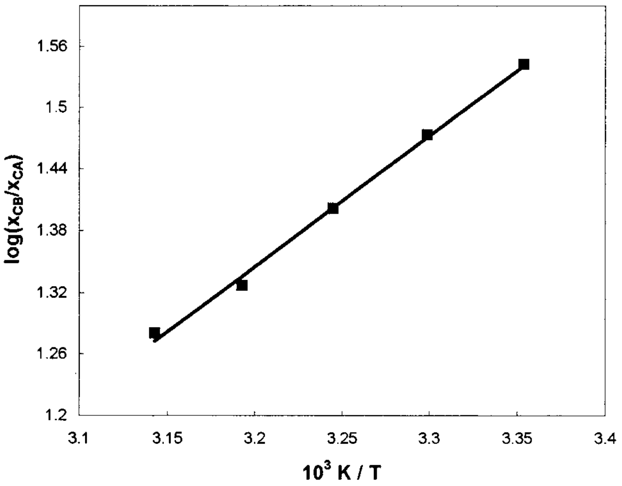

Figure 4. Temperature dependence of the distribution coefficient at infinite dilution for the system water + benzonitrile + propionitrile

Table 3. Solubility Data for the System Water + Propionitrile

t/°C	x_{AA}	x_{CA}	x_{AC}	x_{CC}
25	0.966	0.034	0.151	0.849
30	0.965	0.035	0.164	0.836
35	0.962	0.038	0.179	0.821
40	0.962	0.038	0.196	0.804
45	0.960	0.040	0.236	0.764
50	0.958	0.042	0.264	0.736
55	0.957	0.043	0.297	0.703
60	0.956	0.044	0.321	0.679
65	0.953	0.047	0.346	0.654
70	0.949	0.051	0.365	0.635
75	0.947	0.053	0.390	0.610
80	0.940	0.060	0.409	0.591

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