J. Chem. Eng. Data **1995,** *40,* 1165−1167

Liquid−Liquid Equilibrium Data for Water + Benzonitrile + Ethanol or 1-Propanol

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Liquid−liquid equilibrium for the systems water + benzonitrile + ethanol and water + benzonitrile + 1-propanol have been studied in the temperature range 25−45 °C with analysis by gas chromatography. Phase diagrams, including tie lines and plait points are reported at each temperature. Distribution curves and enthalpy of transfer values of the alcohol from water to the nitrile are also shown.

The use of nitriles as solvents is a subject of continuing interest for the pharmaceutical and fine chemicals industries because of the particular physicochemical properties of these compounds and their capability to intervene in a number of chemical reactions.

In our study of the chemistry and electrochemistry of nitriles it was observed that they react with terpenes *via* a Ritter mechanism, yielding imminium salts which are stable at atmospheric conditions (Caram et al., 1984; Samaniego et al., 1994). Imminium salts obtained from benzonitrile are of particular interest because they show different kinds of biological activity, and thus, an effort was made to evaluate alternative synthesis and purification processes which could be of interest on a production scale.

A literature search indicated little solubility data were published for mixtures containing water and benzonitrile. Thus, in previous work we studied the liquid−liquid equilibrium of the system water + benzonitrile + methanol (Botto et al., 1989). In the present paper our results on the systems water + benzonitrile + ethanol and water + benzonitrile + 1-propanol are reported.

Experimental Section

Bidistilled water and analytical grade benzonitrile (Carlo Erba, 99% purity), ethanol (Merck, 99.8% purity), and 1-propanol (Dorwil, 99% purity) were employed, as received, throughout the experiments. Chromatographic controls carried out on the pure components showed that, in the case of benzonitrile, the impurity concentration was well below 0.05%, while in the case of the alcohols, only minor concentrations of water (around 0.2% in the case of 1-propanol and 0.1% for ethanol) were detected. At this concentration level of water in the alcohols, calibration curves for ethanol and propanol were directly corrected, employing data from the water calibration lines. Thus, as in our previous work (Botto et al., 1989), 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. In the case of ethanol, the column was filled with 10% (volume) FFAP on Chromosorb BW-HP; the initial temperature was 70 °C and was maintained for 5 min before using a 10 K·min^{-1} ramp. The ramp was stopped when the oven temperature reached 170 °C, and this final temperature was maintained for 2 min. The carrier gas was hydrogen, flowing at 35 cm^3·min^{-1}. The injector and detector temperatures were 230 and 200 °C, respectively.

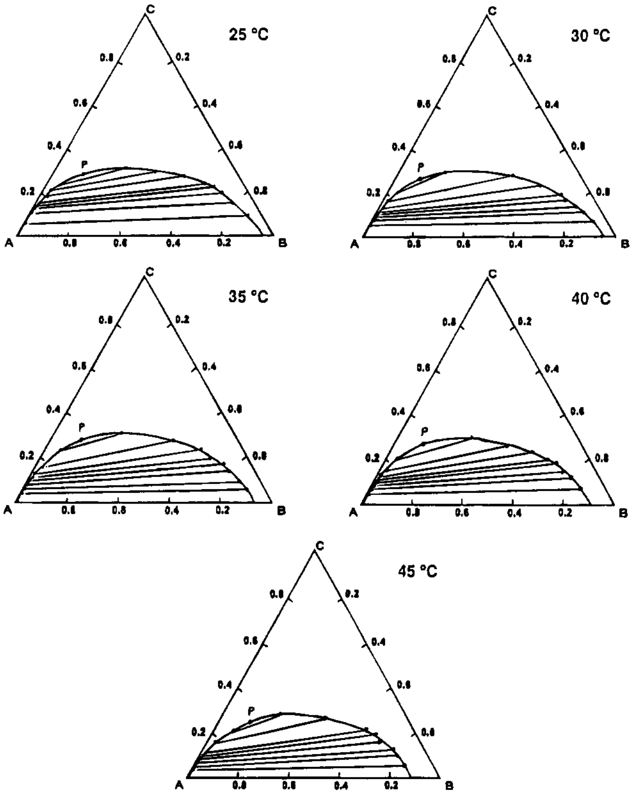

Figure 1. Ternary phase diagrams for the system water + benzonitrile + ethanol at several temperatures.

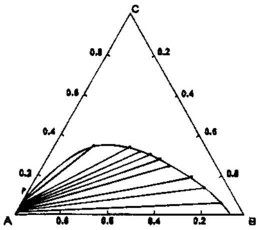

Figure 2. Ternary phase diagram for the system water + benzonitrile + 1-propanol at 35 °C.

In the case of 1-propanol the same experimental characteristics were maintained, except that the column was filled with Porapak Q and the temperature program began at an oven temperature of 200 °C. The same temperature

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0021-9568/95/1740-1165$09.00/0

Table 1. Solubility Data for the System Water (a) + Benzonitrile (b) + Ethanol (c) at Several Temperatures[a]

$x_{a,a}$	$x_{b,a}$	$x_{c,a}$	$x_{a,b}$	$x_{b,b}$	$x_{c,b}$
t = 25 °C					
0.944	0.001	0.055	0.057	0.856	0.087
0.885	0.003	0.112	0.081	0.764	0.155
0.861	0.006	0.133	0.108	0.694	0.198
0.853	0.007	0.140	0.124	0.642	0.234
0.842	0.010	0.148	0.141	0.621	0.238
0.801	0.017	0.182	0.225	0.502	0.273
0.764	0.024	0.212	0.328	0.377	0.295
0.708	0.051	0.241	0.446	0.244	0.310
0.600*	0.115*	0.285*	0.600*	0.115*	0.285*
t = 30 °C					
0.946	0.001	0.053	0.062	0.870	0.068
0.919	0.002	0.079	0.081	0.809	0.110
0.905	0.003	0.092	0.093	0.770	0.137
0.889	0.004	0.107	0.123	0.708	0.169
0.881	0.005	0.114	0.119	0.690	0.191
0.859	0.008	0.133	0.183	0.578	0.239
0.830	0.012	0.158	0.265	0.455	0.280
0.760	0.030	0.210	0.421	0.301	0.278
0.613*	0.112*	0.275*	0.613*	0.112*	0.275*
t = 35 °C					
0.956	0.002	0.042	0.072	0.873	0.055
0.937	0.002	0.061	0.078	0.835	0.087
0.913	0.004	0.083	0.099	0.763	0.134
0.895	0.005	0.100	0.118	0.711	0.171
0.882	0.006	0.112	0.154	0.653	0.193
0.866	0.007	0.127	0.178	0.592	0.230
0.825	0.019	0.156	0.269	0.464	0.267
0.712	0.055	0.233	0.448	0.246	0.306
0.625*	0.110*	0.265*	0.625*	0.110*	0.265*
t = 40 °C					
0.948	0.002	0.050	0.105	0.830	0.065
0.925	0.003	0.072	0.121	0.758	0.121
0.909	0.004	0.087	0.141	0.713	0.146
0.893	0.005	0.102	0.150	0.665	0.185
0.887	0.007	0.106	0.163	0.645	0.192
0.867	0.011	0.122	0.225	0.549	0.226
0.832	0.023	0.145	0.301	0.444	0.255
0.777	0.030	0.193	0.429	0.284	0.287
0.633*	0.108*	0.259*	0.633*	0.108*	0.259*
t = 45 °C					
0.960	0.002	0.038	0.128	0.816	0.056
0.946	0.003	0.051	0.135	0.761	0.104
0.928	0.003	0.069	0.141	0.731	0.128
0.909	0.004	0.087	0.169	0.664	0.167
0.888	0.008	0.104	0.171	0.626	0.203
0.876	0.015	0.109	0.193	0.593	0.214
0.828	0.020	0.152	0.347	0.387	0.266
0.673	0.097	0.230	0.553	0.168	0.279
0.640*	0.106*	0.254*	0.640*	0.106*	0.254*

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

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

$x_{a,a}$	$x_{b,a}$	$x_{c,a}$	$x_{a,b}$	$x_{b,b}$	$x_{c,b}$
t = 25 °C					
0.983	0.002	0.015	0.075	0.856	0.069
0.979	0.003	0.018	0.115	0.749	0.136
0.967	0.003	0.030	0.155	0.655	0.190
0.962	0.003	0.035	0.213	0.541	0.246
0.955	0.003	0.042	0.230	0.487	0.273
0.952	0.004	0.044	0.266	0.430	0.304
0.950	0.005	0.045	0.293	0.386	0.321
0.947	0.006	0.047	0.332	0.337	0.331
0.928	0.008	0.064	0.486	0.170	0.344
0.895*	0.010*	0.095*	0.895*	0.010*	0.095*
t = 30 °C					
0.989	0.002	0.009	0.076	0.862	0.062
0.973	0.003	0.024	0.117	0.747	0.136
0.967	0.003	0.030	0.145	0.678	0.177
0.958	0.004	0.038	0.227	0.529	0.244
0.954	0.005	0.041	0.262	0.444	0.294
0.950	0.006	0.044	0.298	0.391	0.311
0.944	0.007	0.048	0.342	0.332	0.326
0.923	0.009	0.068	0.516	0.152	0.332
0.895*	0.012*	0.087*	0.895*	0.012*	0.087*
t = 35 °C					
0.985	0.002	0.013	0.081	0.856	0.063
0.978	0.003	0.019	0.125	0.739	0.136
0.971	0.004	0.025	0.149	0.665	0.186
0.959	0.005	0.036	0.222	0.530	0.248
0.948	0.006	0.046	0.344	0.333	0.323
0.935	0.007	0.058	0.521	0.145	0.334
0.924	0.009	0.067	0.788	0.068	0.144
0.902*	0.013*	0.085*	0.902*	0.013*	0.085*
t = 40 °C					
0.989	0.003	0.008	0.128	0.768	0.104
0.978	0.003	0.017	0.135	0.735	0.130
0.972	0.004	0.024	0.167	0.650	0.183
0.965	0.004	0.031	0.244	0.513	0.243
0.959	0.004	0.037	0.292	0.418	0.290
0.955	0.005	0.040	0.328	0.368	0.304
0.951	0.006	0.043	0.362	0.305	0.333
0.938	0.007	0.055	0.518	0.152	0.330
0.905*	0.015*	0.080*	0.905*	0.015*	0.080*
t = 45 °C					
0.986	0.003	0.011	0.139	0.782	0.079
0.978	0.004	0.018	0.170	0.695	0.135
0.972	0.004	0.024	0.206	0.602	0.192
0.967	0.005	0.028	0.227	0.532	0.241
0.958	0.006	0.036	0.283	0.418	0.299
0.951	0.007	0.042	0.386	0.282	0.332
0.940	0.008	0.052	0.528	0.151	0.321
0.931	0.009	0.060	0.548	0.140	0.312
0.910*	0.017*	0.073*	0.910*	0.017*	0.073*

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

ramp was used and stopped when the oven temperature reached 230 °C. This final temperature was maintained for 10 min.

Calibration measurements carried out on pure components and homogeneous mixtures showed that benzonitrile, ethanol, and 1-propanol mole fractions could be determined with an accuracy better than 0.001 while, for water, the accuracy was found to be better than 0.002.

Results and Discussion

Liquid–liquid equilibrium data were obtained for both systems at 25, 30, 35, 40, and 45 °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. 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). The obtained data were employed for drawing the phase diagrams of these systems. In Figure 1, ternary diagrams for the case of ethanol are shown at the five temperatures. The general behavior of the system containing 1-propanol with temperature is quite similar to that of ethanol, and thus, in Figure 2 only the diagram corresponding to 35 °C is shown.

log–log distribution curves were plotted for both systems, and in Figures 3 and 4, typical results are shown. The slope of the straight lines obtained is close to 1 in both cases, which indicates that no association occurs. Finally, the theoretical dependence of the distribution coefficient,

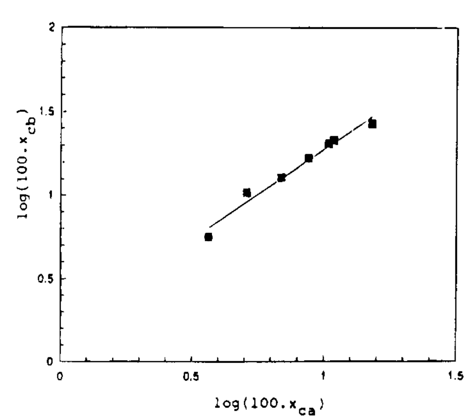

Figure 3. Distribution curve for the system water + benzonitrile + ethanol at 45 °C.

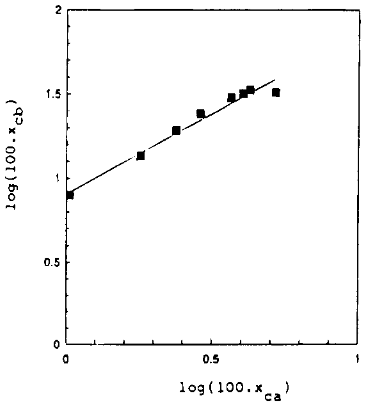

Figure 4. Distribution curve for the system water + benzonitrile + 1-propanol at 45 °C.

m_c, with temperature is given by

$$\log m_c = [(H_{c,a} - H_{c,b})/2.3RT] + K$$

where $H_{c,a}$ and $H_{c,b}$ are, respectively, the partial molar heat contents of the alcohol in water and benzonitrile solutions. Hence, plotting $\log m_c$ *vs* $1/T$ as in Figures 5 and 6 allows the molar enthalpy change for transferring the alcohol from the benzonitrile rich phase to the water rich phase to be obtained. The obtained value is -19.3 kJ·mol^{-1} for the case of ethanol and -37.5 kJ·mol^{-1} for 1-propanol. When these values are compared with the molar enthalpy change for transferring methanol from water to benzonitrile, which was previously found to be -13.4 kJ·mol^{-1} (Botto et al., 1989), it is seen that, as should be expected, the exothermicity of alcohol transfer from water to benzonitrile increases as the alcohol molecule becomes less polar.

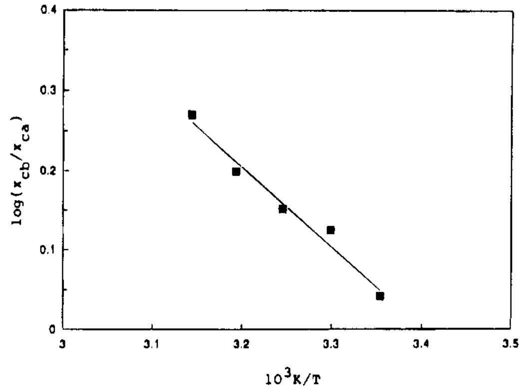

Figure 5. Temperature dependence of the distribution coefficient for the systema water + benzonitrile + ethanol.

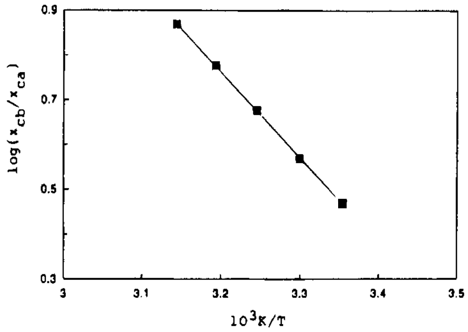

Figure 6. Temperature dependence of the distribution coefficient for the system water + benzonitrile + 1-propanol.

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Received for review January 9, 1995. Revised May 24, 1995. Accepted July 19, 1995.®

JE950005P

® Abstract published in *Advance ACS Abstracts,* September 1, 1995.