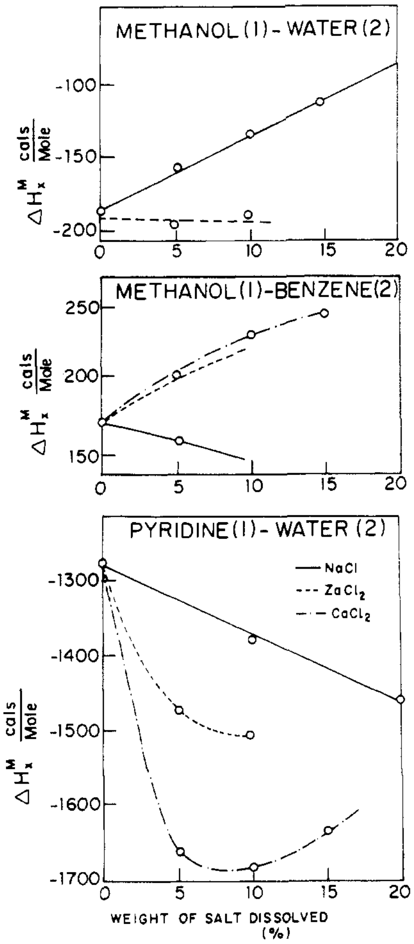

Figure 6. Effect of salts on equimolal concentration.

have increased when all three salts are used. This can be attributed to the further strengthening of hydrogen bonding in the presence of dissolved salts.

Conclusion

In conclusion it can be stated that like relative volatility of solvent in VLE and selectivity of a solute in liquid-liquid equilibria, the enthalpy change on mixing of two solvents is also likely to be influenced by the addition of salts to solvent mixtures. As mentioned earlier, this work has been mainly of an exploratory nature.

Glossary

ΔH_x^M	heat of mixing, cal/mol
V	potential drop across the heating coil, V
I	current passing through the heating coil, A
t	time, s
x_i	liquid-phase composition of component i, mole fraction
A_0, A_1, A_2, ...	binary constants in Scatchard model (eq 1)
1, 2	components 1 and 2

Abbreviations

VLE	vapor-liquid equilibria
LLE	liquid-liquid equilibria

Registry No. NaCl, 7647-14-5; $CaCl_2$, 10043-52-4; $ZnCl_2$, 7646-85-7; MeOH, 67-56-1; benzene, 71-43-2; pyridine, 110-86-1.

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Liquid–Liquid Equilibrium Data for the System Water–Benzonitrile–Methanol

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Liquid–liquid equilibrium data for the system water–benzonitrile–methanol have been obtained at several temperatures by employing gas chromatography for chemical analysis. The obtained results show that there is no association of methanol molecules in benzonitrile.

Nonaqueous solvents are of increasing importance in industrial processes. Among them, nitriles play a very significant role because of their outstanding physicochemical properties (large dielectric constant, low vapor pressure, good electrochemical stability) and, also, because they intervene in a number of reactions, particularly in regard to the obtention of pharmaceutical drugs.

Economical use of nitriles in industry requires efficient ways for their recovery, and since in a number of cases distillation is not useful, or might even be dangerous, alternative separation processes must be considered. Solvent extraction seems to be a reasonable choice, but the lack of data on ternary equi-

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Table I. Molar Fractions of Water, Benzonitrile, and Methanol in Both Phases at 25 °C

X_{A1}	X_{B1}	X_{C1}	X_{A2}	X_{B2}	X_{C2}
0.881	0.005	0.114	0.106	0.845	0.049
0.821	0.005	0.174	0.106	0.795	0.099
0.781	0.010	0.209	0.111	0.770	0.119
0.742	0.010	0.248	0.117	0.730	0.153
0.692	0.015	0.293	0.127	0.690	0.183
0.657	0.015	0.328	0.137	0.635	0.228
0.603	0.025	0.372	0.143	0.620	0.237
0.548	0.050	0.402	0.148	0.605	0.247

Table II. Molar Fractions of Water, Benzonitrile, and Methanol in Both Phases at 30 °C

X_{A1}	X_{B1}	X_{C1}	X_{A2}	X_{B2}	X_{C2}
0.916	0.005	0.079	0.121	0.830	0.049
0.866	0.005	0.129	0.126	0.795	0.079
0.816	0.010	0.174	0.141	0.750	0.109
0.762	0.015	0.223	0.147	0.720	0.133
0.712	0.020	0.268	0.147	0.695	0.158
0.672	0.025	0.303	0.162	0.650	0.188
0.623	0.035	0.342	0.173	0.600	0.227
0.583	0.050	0.367	0.178	0.575	0.247
0.523	0.085	0.392	0.198	0.535	0.267

Table III. Molar Fractions of Water, Benzonitrile, and Methanol in Both Phases at 35 °C

X_{A1}	X_{B1}	X_{C1}	X_{A2}	X_{B2}	X_{C2}
0.926	0.005	0.069	0.126	0.835	0.039
0.881	0.010	0.109	0.136	0.795	0.069
0.846	0.015	0.139	0.141	0.770	0.089
0.812	0.020	0.168	0.147	0.735	0.118
0.767	0.025	0.208	0.152	0.715	0.133
0.737	0.025	0.238	0.157	0.700	0.143
0.713	0.030	0.257	0.163	0.690	0.147
0.633	0.050	0.317	0.173	0.640	0.187
0.553	0.070	0.377	0.183	0.585	0.232

libria involving these compounds imposes a first constraint for design calculations.

In view of this, it was decided to begin experimental work in order to obtain liquid–liquid equilibrium data for A–B–C systems in which B is a nitrile. Our first choice was benzonitrile, because of its considerable importance in pharmaceutical chemistry and, also, on account of the lack of published data. In fact, a literature search showed only two papers (*1*, *2*) in which just the solubility curves for the systems acetonitrile–benzonitrile–water and methanol–benzonitrile–water are given at a single temperature while the corresponding tie lines are not determined.

Thus, taking into account that water is the most common impurity in benzonitrile once the chemical reactions are completed and, as the beginning of a systematic effort, the system water (A)–benzonitrile (B)–methanol (C) was studied at different temperatures. The obtained results are reported in this paper.

Experimental Section

Bidistilled water and analytical grade benzonitrile and methanol were employed throughout the experiments. Chromatographic analysis showed that water and benzonitrile were essentially free from impurities, while methanol had only very minor amounts of water. Since quantitative analysis was based on water and benzonitrile determination in weighed samples, this fact was not a problem in determining the precise composition of both phases in each experiment. Solutions were prepared in glass tubes and thermostated to 0.1 °C until the two phases were in equilibrium. Chemical analysis of each phase was performed by gas chromatography, employing a Porapak-Q

Table IV. Molar Fractions of Water, Benzonitrile, and Methanol in Both Phases at 40 °C

X_{A1}	X_{B1}	X_{C1}	X_{A2}	X_{B2}	X_{C2}
0.921	0.010	0.069	0.161	0.790	0.049
0.846	0.015	0.139	0.171	0.750	0.079
0.791	0.025	0.184	0.176	0.720	0.104
0.742	0.040	0.218	0.182	0.695	0.123
0.702	0.045	0.253	0.187	0.660	0.153
0.622	0.070	0.308	0.212	0.580	0.208
0.583	0.080	0.337	0.218	0.550	0.232
0.548	0.090	0.362	0.223	0.515	0.262
0.513	0.105	0.382	0.233	0.495	0.272

Table V. Molar Fractions of Water, Benzonitrile, and Methanol in Both Phases at 45 °C

X_{A1}	X_{B1}	X_{C1}	X_{A2}	X_{B2}	X_{C2}
0.916	0.015	0.069	0.191	0.760	0.049
0.801	0.025	0.174	0.201	0.695	0.104
0.766	0.035	0.199	0.206	0.665	0.129
0.742	0.040	0.218	0.212	0.640	0.148
0.707	0.045	0.248	0.217	0.615	0.168
0.672	0.050	0.278	0.222	0.590	0.188
0.633	0.065	0.302	0.243	0.550	0.207
0.593	0.075	0.332	0.248	0.505	0.247
0.563	0.090	0.347	0.263	0.480	0.257

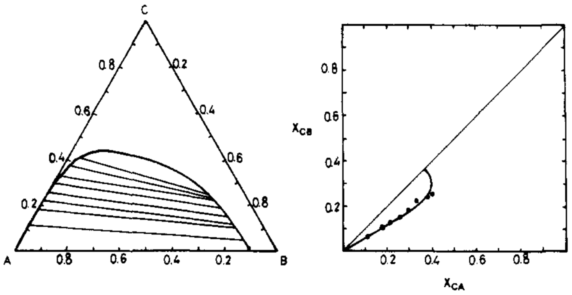

Figure 1. Ternary equilibrium diagram and distribution curve for the system water–benzonitrile–methanol at 25 °C.

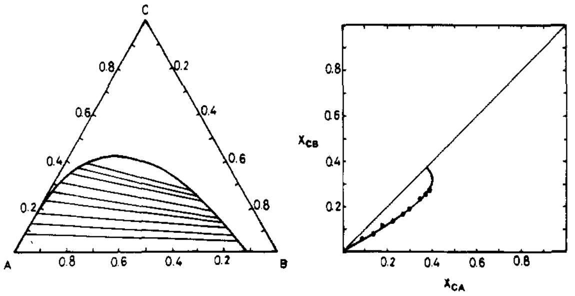

Figure 2. Ternary equilibrium diagram and distribution curve for the system water–benzonitrile–methanol at 30 °C.

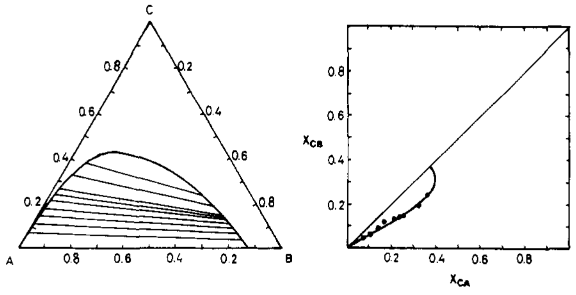

Figure 3. Ternary equilibrium diagram and distribution curve for the system water–benzonitrile–methanol at 35 °C.

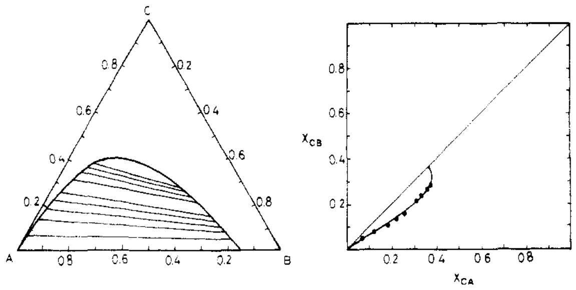

Figure 4. Ternary equilibrium diagram and distribution curve for the system water-benzonitrile-methanol at 40 °C.

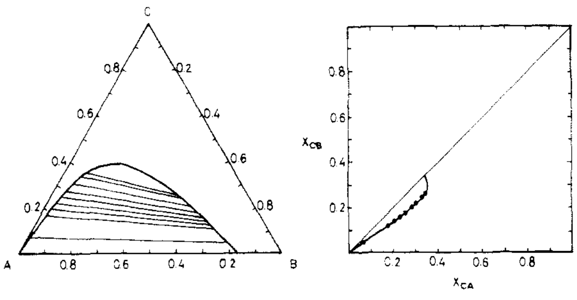

Figure 5. Ternary equilibrium diagram and distribution curve for the system water-benzonitrile-methanol at 45 °C.

column and an adequate temperature program with a carrier gas flow rate of 60 mL/min.

Results and Discussion

Liquid-liquid equilibria for the system under study were characterized at 25, 30, 35, 40, and 45 °C. Composition data are shown in Tables I-V and the obtained ternary diagrams are displayed in Figures 1-5, together with the corresponding distribution curves. Molar fractions were employed throughout the calculations, and are expressed as X_{in}, where the first index refers to the component (A, B, or C) and the second to the phase (1, water-rich phase; 2, benzonitrile-rich phase). Plait points were determined by the method of Hand (*3*).

The shape of the obtained curves clearly shows that methanol, and probably all highly polar alcohols, is not an adequate solvent for extracting water from the benzonitrile-rich phase. However, some interesting conclusions may be drawn from these data.

Thus, plots of X_{C2} vs X_{C1} are reasonably linear up to 0.2–0.3 values, suggesting that methanol does not associate in benzonitrile. This conclusion is further supported by the fact that log X_{C2} vs log X_{C1} (Figure 6) plots display a slope of 1.1, instead of 0.5 as should be expected for the case of methanol association.

From another point of view, the theoretical dependence of the distribution coefficient with temperature is given by

$$\log m_C = (H_{C1} - H_{C2})/2.3RT + K$$

where H_{C1} and H_{C2} are respectively the partial molar heat contents of methanol in water and benzonitrile. Hence, plotting log m_C vs $1/T$ as in Figure 7 allows obtaining of the molar enthalpy change for transferring methanol from the benzonitrile-rich to the water-rich phase. This value is found to be −3.2 kcal/mol, which points to a slightly exothermic process.

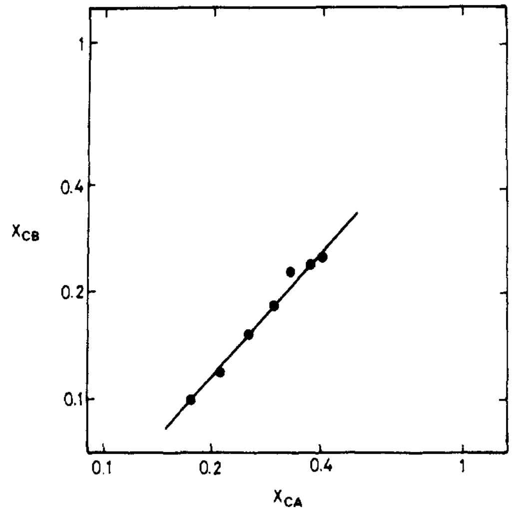

Figure 6. Log-log plot for molar fractions of methanol in benzonitrile-rich and water-rich phases at 25 °C.

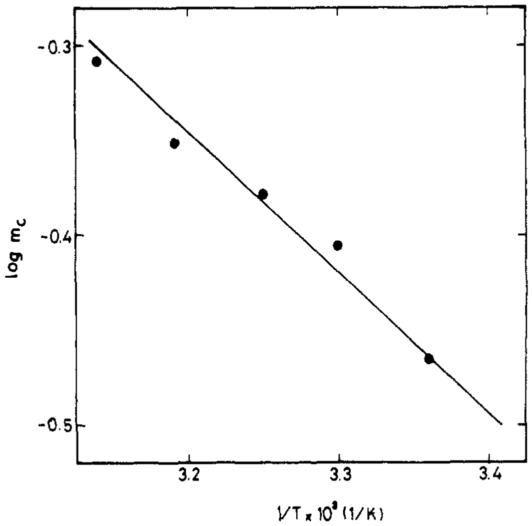

Figure 7. van't Hoff plot for methanol distribution.

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Registry No. PhCN, 100-47-0; MeOH, 67-56-1.

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