J. Chem. Eng. Data **2010,** *55,* 1645–1648

Liquid−Liquid Equilibria for Water + Benzonitrile + *N*-Methylacetamide, or + *N*,*N*-Dimethylacetamide

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Liquid−liquid equilibria for the systems water + benzonitrile + *N*-methylacetamide and water + benzonitrile + *N*,*N*-dimethylacetamide were measured in the temperature range of (288.15 to 328.15) K at atmospheric pressure. Phase diagrams, including binodal curves and tie lines, are reported for both systems at each temperature. The plait point compositions have been calculated by Hand's method. Enthalpy changes for the transfer of the substituted acetamide from benzonitrile to water are given.

Introduction

Benzonitrile (C_6H_5CN) is generally a good solvent for the study of organic, anhydrous inorganic, and organometallic compounds. It is generally similar in its behavior as a solvent to acetonitrile (CH_3CN). However, one important structural difference between the two solvents is that bezonitrile does not have a labile hydrogen atom in the α position to the nitrile. The lack of an α-hydrogen potentially allows for stabilization of species that would react with acetonitrile.

Benzonitrile (BZN) has a relatively large dipole moment for an aromatic solvent, and the relative permittivity of 25.20 is also large compared to most other aromatic solvents, has a low vapor pressure, and hence is a good solvent to use when there is the possibility of concentration changes due to evaporation.

BZN compounds are also of interest. Thus, in previous work it has been found that iminium salts obtained by reaction of BZN with terpenes[1,2] show interesting physical and biological properties, and more recently, BZN is becoming important in the synthesis of alkyl benzonitrile derivatives of calyx[4]arene[3] that can be used for contaminated groundwater and industrial effluents remediation. Thus, the development of extractive methods for recovery of the nitrile is an important issue.

Continuing our systematic work on phase equilibria in ternary mixtures containing water, BZN, and a third component,[4−9] liquid−liquid equilibrium (LLE) data for the systems water + BZN + *N*-methylacetamide and water + BZN + *N*,*N*-dimethylacetamide in the temperature range (288.15 to 328.15) K were obtained and are reported here. The influence of the temperature on the liquid−liquid equilibria has been studied for both systems.

Experimental Section

Bidistilled, deionized water with a conductance below 1 $\mu S\cdot cm^{-1}$ obtained from a Millipore Milli-Q type equipment was employed. Merck chromatographic grade, BZN (99.86 % mass fraction), *N*-methylacetamide (99.85 % mass fraction), and *N*,*N*-dimethylacetamide (99.85 % mass fraction) were used as received. No further purification was attempted since the claimed purity grade was checked by gas chromatography (GC), and no water traces were detected in these analyses.

Mixtures of at least 50 g each were prepared in small glass flasks employing a balance (Mettler H20−332131) with an uncertainty of 10^{-5} g. The flasks were placed in a water bath controlled to ± 0.1 K by means of a thermostat (Lauda E-200). The mixtures were continuously stirred for a period of 10 min, by means of a magnetic bar, and then allowed to rest for at least 2 h. At the end of the setting period, samples were collected from both phases with a 10 μL syringe for GC analysis until three consecutive measurements yielded coincident results within experimental uncertainty.

The compositions of the sampled liquid phases, for both systems, were determined by GC employing a Konik HRGC - 3000 chromatograph, equipped with a thermal conductivity detector (TCD). Stainless steel columns of 0.32 cm diameter and 2 m long were employed. The carrier gas was hydrogen, flowing at 36 $cm^3\cdot min^{-1}$. Injector and detector temperatures were (473.15 and 493.15) K, respectively.

In the case of the system water + BZN + *N*-methylacetamide, the column was filled with 10 % (volume) FFAP on Chromosorb BW-HP. The initial temperature was 403.15 K and was maintained for 3 min before setting on a 20 $K\cdot min^{-1}$ ramp. The temperature ramp was stopped at 463.15 K, and this final temperature was maintained for 2 min. In the case of the system water + BZN + *N*,*N*-dimethylacetamide, the column was filled with 15 % (volume) Carbowax 20 M on Chromosorb W-AW-DMCS. The temperature program began with an initial temperature of 363.15 K that was maintained for 3 min, and then a 20 $K\cdot min^{-1}$ ramp was started. When the oven temperature reached 443.15 K, the ramp was stopped, and the final temperature was maintained for 2 min.

The internal normalization method employing response factors was used in the calibration process.[10] In doing this, five samples were prepared in the organic-rich, one-phase region, and the resulting relative constants were plotted as a function of relative composition. Two samples were prepared in the water-rich, one-phase zone where no differences were found in the relative constants. Calibration coefficients were obtained by fitting a straight line to the calibration results for each composition range. The calibration equations were used to convert the

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10.1021/je9007074

Table 1. Tie-Line Data for the System Water (A) + Benzonitrile (B) + *N*-Methylacetamide (C) at Several Temperatures[a]

water-rich phase			benzonitrile-rich phase		
x_{AA}	x_{BA}	x_{CA}	x_{AB}	x_{BB}	x_{CB}
$T = 288.15$ K					
0.8818	0.0033	0.1149	0.0136	0.9754	0.0111
0.8002	0.0060	0.1938	0.0156	0.9534	0.0310
0.7332	0.0108	0.2560	0.0171	0.9337	0.0492
0.6550	0.0202	0.3247	0.0193	0.9083	0.0724
0.5996	0.0322	0.3682	0.0199	0.8852	0.0949
0.5444	0.0435	0.4121	0.0215	0.8591	0.1195
0.5006	0.0562	0.4432	0.0231	0.8323	0.1446
0.4400	0.0849	0.4751	0.0250	0.8000	0.1751
0.3860	0.1181	0.4959	0.0321	0.7534	0.2145
0.2227	0.2669	0.5104	0.0427	0.7152	0.2422
0.0681*	0.6021*	0.3298*	0.0681*	0.6021*	0.3298*
$T = 298.15$ K					
0.8836	0.0061	0.1104	0.0351	0.9498	0.0151
0.7988	0.0090	0.1922	0.0375	0.9285	0.0341
0.7389	0.0130	0.2481	0.0386	0.9094	0.0520
0.6658	0.0225	0.3117	0.0399	0.8836	0.0765
0.6083	0.0353	0.3565	0.0460	0.8535	0.1005
0.5460	0.0507	0.4033	0.0485	0.8166	0.1349
0.5050	0.0652	0.4298	0.0513	0.7927	0.1560
0.4409	0.1002	0.4589	0.0555	0.7593	0.1852
0.3793	0.1401	0.4806	0.0621	0.7084	0.2296
0.3224	0.1852	0.4924	0.0698	0.6632	0.2670
0.1003*	0.5495*	0.3502*	0.1003*	0.5495*	0.3502*
$T = 308.15$ K					
0.8824	0.0079	0.1097	0.0597	0.9174	0.0228
0.8090	0.0111	0.1799	0.0625	0.8979	0.0395
0.7489	0.0156	0.2355	0.0663	0.8763	0.0574
0.6845	0.0243	0.2912	0.0650	0.8503	0.0848
0.6127	0.0384	0.3489	0.0665	0.8175	0.1160
0.5613	0.0547	0.3840	0.0685	0.7885	0.1430
0.5160	0.0709	0.4131	0.0701	0.7586	0.1713
0.4532	0.1041	0.4428	0.0752	0.7242	0.2006
0.3948	0.1421	0.4630	0.0819	0.6783	0.2398
0.3274	0.1996	0.4730	0.0955	0.6055	0.2989
0.1281*	0.5079*	0.3640*	0.1281*	0.5079*	0.3640*
$T = 318.15$ K					
0.8998	0.0087	0.0915	0.0975	0.8738	0.0286
0.8320	0.0122	0.1558	0.0978	0.8512	0.0510
0.7695	0.0175	0.2130	0.0973	0.8275	0.0752
0.6988	0.0270	0.2742	0.0975	0.7934	0.1091
0.6396	0.0401	0.3204	0.0984	0.7565	0.1452
0.5753	0.0608	0.3639	0.0979	0.7198	0.1823
0.5396	0.0771	0.3833	0.0991	0.7004	0.2005
0.4974	0.0975	0.4051	0.1020	0.6668	0.2312
0.4368	0.1356	0.4275	0.1109	0.6152	0.2740
0.3509	0.1948	0.4543	0.1250	0.5550	0.3200
0.1641*	0.4550*	0.3808*	0.1641*	0.4550*	0.3808*
$T = 328.15$ K					
0.9247	0.0092	0.0661	0.1066	0.8638	0.0296
0.8530	0.0140	0.1329	0.1070	0.8318	0.0612
0.7794	0.0205	0.2001	0.1088	0.7912	0.1001
0.7084	0.0302	0.2614	0.1097	0.7500	0.1402
0.6569	0.0426	0.3004	0.1108	0.7140	0.1752
0.5947	0.0648	0.3405	0.1121	0.6796	0.2083
0.5606	0.0784	0.3610	0.1139	0.6512	0.2350
0.5058	0.1006	0.3936	0.1235	0.6018	0.2747
0.4380	0.1456	0.4164	0.1274	0.5738	0.2989
0.3380	0.2199	0.4421	0.1491	0.5112	0.3398
0.1922*	0.4182*	0.3896*	0.1922*	0.4182*	0.3896*

[a] Asterisks correspond to plait points.

Table 2. Tie-Line Data for the System Water (A) + Benzonitrile (B) + *N*,*N*-Dimethylacetamide (C) at Several Temperatures[a]

water-rich phase			benzonitrile-rich phase		
x_{AA}	x_{BA}	x_{CA}	x_{AB}	x_{BB}	x_{CB}
$T = 288.15$ K					
0.9566	0.0041	0.0393	0.0268	0.9336	0.0396
0.9170	0.0065	0.0765	0.0371	0.8753	0.0877
0.8709	0.0118	0.1173	0.0521	0.8040	0.1439
0.8434	0.0143	0.1423	0.0689	0.7486	0.1825
0.8023	0.0215	0.1762	0.0805	0.6962	0.2234
0.7792	0.0251	0.1957	0.1006	0.6502	0.2492
0.7487	0.0312	0.2201	0.1236	0.5964	0.2799
0.7233	0.0366	0.2401	0.1426	0.5569	0.3004
0.6916	0.0427	0.2657	0.1737	0.4955	0.3308
0.6230	0.0750	0.3020	0.3020	0.3290	0.3690
0.4897*	0.1401*	0.3702*	0.4897*	0.1401*	0.3702*
$T = 298.15$ K					
0.9583	0.0055	0.0361	0.0495	0.9075	0.0430
0.9158	0.0092	0.0750	0.0652	0.8383	0.0965
0.8895	0.0123	0.0983	0.0795	0.7892	0.1313
0.8477	0.0172	0.1351	0.0901	0.7217	0.1882
0.8196	0.0215	0.1590	0.1006	0.6800	0.2193
0.7982	0.0263	0.1755	0.1162	0.6424	0.2414
0.7681	0.0323	0.1996	0.1373	0.5913	0.2714
0.7226	0.0454	0.2320	0.1924	0.4955	0.3121
0.6988	0.0508	0.2505	0.2125	0.4577	0.3298
0.6630	0.0649	0.2721	0.2711	0.3817	0.3472
0.5270*	0.1349*	0.3381*	0.5270*	0.1349*	0.3381*
$T = 308.15$ K					
0.9576	0.0073	0.0351	0.0799	0.8711	0.0490
0.9289	0.0099	0.0612	0.0875	0.8227	0.0898
0.9012	0.0128	0.0860	0.0968	0.7711	0.1320
0.8862	0.0154	0.0984	0.1049	0.7426	0.1525
0.8540	0.0199	0.1261	0.1152	0.6864	0.1983
0.8018	0.0318	0.1664	0.1524	0.5877	0.2599
0.7685	0.0411	0.1904	0.1948	0.5151	0.2901
0.7372	0.0520	0.2108	0.2306	0.4592	0.3102
0.7177	0.0564	0.2259	0.2601	0.4107	0.3293
0.6898	0.0651	0.2451	0.3356	0.3219	0.3425
0.5599*	0.1303*	0.3098*	0.5599*	0.1303*	0.3098*
$T = 318.15$ K					
0.9605	0.0097	0.0298	0.1006	0.8495	0.0499
0.9396	0.0125	0.0479	0.1007	0.8161	0.0832
0.9157	0.0149	0.0695	0.1120	0.7669	0.1210
0.8966	0.0181	0.0853	0.1211	0.7278	0.1512
0.8826	0.0204	0.0970	0.1250	0.7030	0.1721
0.8595	0.0251	0.1155	0.1448	0.6497	0.2055
0.8350	0.0294	0.1356	0.1752	0.5775	0.2473
0.8001	0.0377	0.1622	0.2007	0.5242	0.2751
0.7513	0.0522	0.1965	0.2650	0.4230	0.3120
0.7076	0.0675	0.2250	0.3249	0.3401	0.3350
0.6008*	0.1187*	0.2805*	0.6008*	0.1187*	0.2805*
$T = 328.15$ K					
0.9637	0.0102	0.0261	0.1176	0.8323	0.0500
0.9492	0.0128	0.0381	0.1221	0.7981	0.0799
0.9264	0.0165	0.0571	0.1322	0.7463	0.1215
0.9041	0.0205	0.0755	0.1479	0.6872	0.1650
0.8765	0.0248	0.0987	0.1641	0.6327	0.2032
0.8555	0.0282	0.1162	0.1848	0.5815	0.2337
0.8300	0.0351	0.1348	0.2181	0.5181	0.2638
0.8067	0.0401	0.1532	0.2478	0.4647	0.2876
0.7787	0.0502	0.1711	0.2816	0.4130	0.3054
0.7474	0.0598	0.1928	0.3429	0.3324	0.3247
0.6354*	0.1152*	0.2494*	0.6354*	0.1152*	0.2494*

[a] Asterisks correspond to plait points.

area fraction into mass fraction, and the mole fraction was calculated from the mass fraction. The detection limit for each component was established as the amount at which the peak intensity doubles the standard deviation. In all cases, the limit is below 1 μg. Therefore, the mole fractions have an uncertainty of ± 0.0002.

Results and Discussion

The liquid−liquid phase diagrams for both systems are of type I,[11] where only one binary subsystem has a very low partial miscibility and two binary subsystems are miscible.

The composition of the liquid phases at equilibrium was determined in the temperature range of (288.15 to 328.15) K,

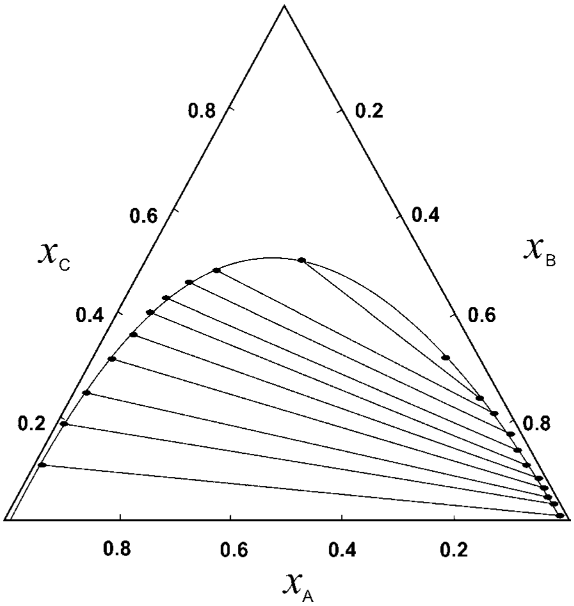

Figure 1. Ternary phase diagram for the system water (A) + benzonitrile (B) + *N*-methylacetamide (C) at 288.15 K.

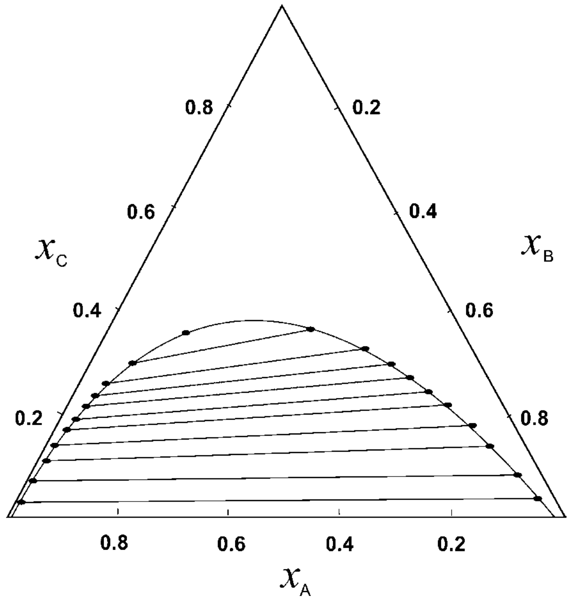

Figure 2. Ternary phase diagram for the system water (A) + benzonitrile (B) + *N*,*N*-dimethylacetamide (C) at 288.15 K.

at atmospheric pressure, for both systems. Obtained data are presented in Tables 1 and 2. In these tables composition values corresponding to plait points, as determined by the method of Hand,[12] are also included. Compositions are always expressed in mole fractions, $x_{i,A}$ and $x_{i,B}$, where the first index refers to the component (A = water, B = benzonitrile, C = *N*-methylacetamide or *N*,*N*-dimethylacetamide) and the second refers to the phase (A = water-rich phase, B = benzonitrile-rich phase). The general shape of the ternary diagram for each system is the same at all temperatures. Typical curves, which correspond to equilibria at 288.15 K, can be seen in Figures 1 and 2 for both systems.

The temperature has a gradual effect on the size of immiscibility region in the investigated temperature range. The area corresponding to the heterogeneous region diminishes with increasing temperature, in both systems, so increasing temperature increases the mutual solubility between benzonitrile and water.

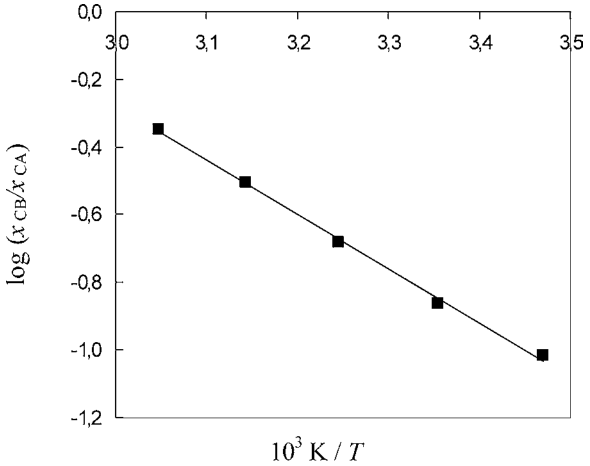

Figure 3. Temperature dependence of the logarithm of the distribution coefficient at infinite dilution, log(x_{CB}/x_{CA}), for the system water + benzonitrile + *N*-methylacetamide.

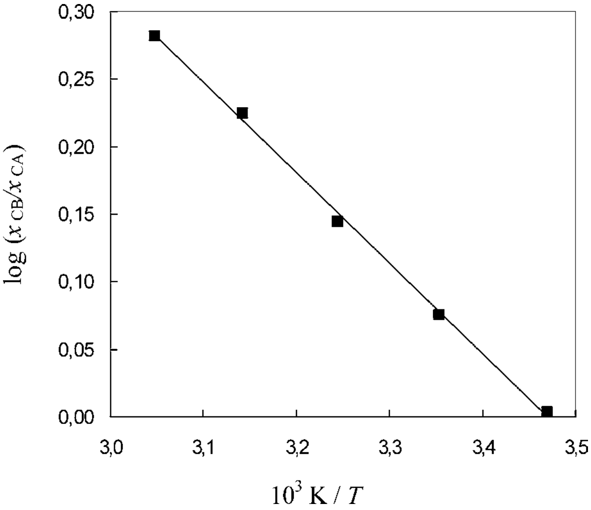

Figure 4. Temperature dependence of the logarithm of the distribution coefficient at infinite dilution, log(x_{CB}/x_{CA}), for the system water + benzonitrile + *N*,*N*-dimethylacetamide.

It can be observed, in the comparative study of the liquid−liquid phase diagrams, that in the case of the ternary system with *N*,*N*-dimethylacetamide it shows a smaller extension to the two-phase region, at a same temperature, than the case of the ternary system with *N*,*N*-dimethylacetamide. So, *N*,*N*-dimethylacetamide is more soluble in the system containing water + benzonitrile than the *N*-methylacetamide. Similar results were obtained for the relative solubilities of the *N*,*N*-dimethylformamide from *N*-methylformamide in the system containing water + benzonitrile.[7] Besides, the substituted formamides are more soluble in the system containing water + benzonitrile than the sustituted acetamides.

As seen from the slopes of the tie lines of both systems, *N*-methylacetamide is more soluble in the water-rich phase than in the BZN-rich phase, while the opposite occurs in the case of *N*,*N*-dimethylacetamide.

This behavior can be explained from the fact that in the *N*,*N*-dimethylacetamide molecule the free electron pair on the nitrogen atom is hindered by two methyl groups, while in the case of *N*-methylacetamide this electron pair is protected by a single methyl group allowing it to interact with the hydrogen atoms of the water.

Finally, the theoretical dependence of the distribution coefficient at infinite dilution,[12] $m_C = x_{C,B}/x_{C,A}$, with temperature is given by

$$\begin{aligned}\log m_C &= [(H_{C,A} - H_{C,B})/2.303RT] + K \\ &= \Delta H_{tr}/2.303RT + K\end{aligned}$$

where $H_{C,A}$ and $H_{C,B}$ are, respectively, the partial molar enthalpies of the substituted acetamide in water and in benzonitrile solutions and ΔH_{tr} is the enthalpy of transfer of the substituted acetamide from the benzonitrile-rich phase to the water-rich phase. Plotting $\log m_C$ vs $1/T$ allows us to obtain this value. To calculate the enthalpy of transfer at infinite dilution, the mole fractions of the substituted acetamide in the water-rich phase were plotted as a function of the mole fractions in the benzonitrile-rich phase, and the resulting points were fitted to a fourth degree polynomial, whose slope at the origin gives the distribution coefficient at infinite dilution.

In both cases, the enthalpy of transfer of the substituted acetamide from the benzonitrile-rich phase to the water-rich phase was obtained by plotting the logarithm of the distribution coefficient at infinite dilution, m_C, against T^{-1} as shown in Figures 3 and 4. From these plots, the enthalpy of transfer of substituted acetamide, ΔH_{tr}, is -30.6 kJ·mol^{-1} in the case of *N*-methylacetamide and -12.8 kJ·mol^{-1} for *N*,*N*-dimethylacetamide.

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Received for review August 28, 2009. Accepted December 9, 2009.

JE9007074