Liquid−Liquid Equilibria for Water + Benzonitrile + Ethyl Acetate or + Butyl Acetate

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Liquid−liquid equilibria for the systems water + benzonitrile + ethyl acetate and water + benzonitrile (BZN) + butyl acetate were measured in the temperature range of 25 °C to 45 °C. Phase diagrams, including tie lines, are reported for both systems at each temperature. Distribution curves for ethyl acetate and butyl acetate in both phases and enthalpy changes for the transfer of the ester from BZN to water are given. Solubility data for the binaries water + ethyl acetate and water + butyl acetate in the temperature range of 25 °C to 60 °C were also measured.

Introduction

In designing the process for the synthesis of iminium salts obtained from the reaction of benzonitrile (BZN) with terpenes, the development of extractive methods for the recovery of the nitrile is an important issue. In continuation of our systematic work on phase equilibria in ternary mixtures containing water, BZN, and a third component,[1−6] liquid−liquid equilibrium (LLE) data for the systems water + BZN + ethyl acetate and water + BZN + butyl acetate in the 25 °C to 45 °C temperature range were obtained and are reported in this article.

Experimental Section

Bidistilled water and analytical-grade benzonitrile (Carlo Erba, 99% purity), ethyl acetate (Merck, 99.8% purity), and butyl acetate (Aldrich 99.5% purity) were employed as received. Impurities in the three organic solvents were below 0.05% as shown by gas chromatography (GC). Water was not detected in these analyses.

Weighed samples of at least 50 g each were prepared in small glass flasks employing a Mettler H20-332131 balance with an uncertainty of 10^{-5} g. The flasks were placed in a water bath controlled to ±0.1 K by means of a Lauda E-200 thermostat. The samples were continuously stirred for periods of 10 min, by means of a magnetic bar, and then allowed to rest for at least 2 h before samples were collected from both phases with a 10 μL syringe for GC analysis until three consecutive measurements yielded coincident results within experimental error. Thence, it was considered that equilibrium was attained.

Gas chromatography measurements for both systems were carried out with a Konik HRGC-3000 chromatograph employing a stainless steel column of $^1/_8$ in. diameter and 2 m long filled with Porapak Q. A thermal conductivity detector was used. The temperature program began with an initial temperature of 230 °C that was maintained for 3 min, and then a 10 K min^{-1} ramp was started. When the oven temperature reached 240 °C, the ramp was stopped, and the final temperature was maintained for 5 min; hydrogen was employed as the carrier gas flowing at 35 cm^3 min^{-1}. The injector and detector temperatures were 230 °C.

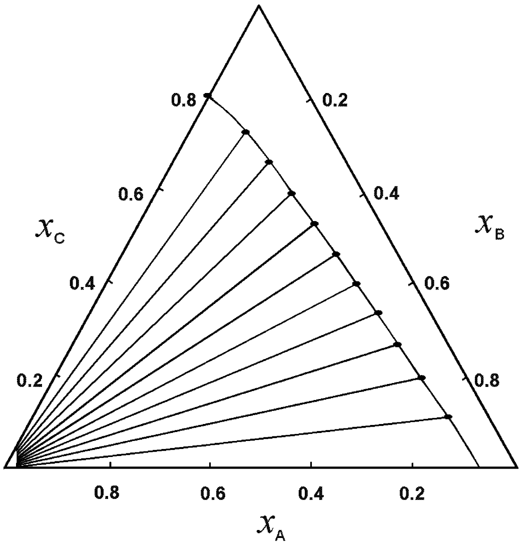

Figure 1. Ternary phase diagram for the system water (A) + benzonitrile (B) + ethyl acetate (C) at 35 °C.

The internal standard approach was employed in the calibration process. 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. The detection limit for each component was established as the amount at which the peak intensity doubles the standard deviation of a sample of the component. In all cases, the limit is below 1 μg. Therefore, the molar fractions have an uncertainty of ±0.0001.

Results and Discussion

LLE data obtained for both systems in the temperature range of 25 °C to 45 °C are shown in Tables 1 and 2. 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 = ethyl acetate or butyl acetate) and the second refers to the phase (A = water-rich phase, B = benzonitrile-rich phase). The general shape of the ternary

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Table 1. Tie-Line Data for the System Water (A) + Benzonitrile (B) + Ethyl Acetate (C) at Several Temperatures

water-rich phase						benzonitrile-rich phase					
x_{AA}	x_{BA}	x_{CA}	x_{AA}	x_{BA}	x_{CA}	x_{AB}	x_{BB}	x_{CB}	x_{AB}	x_{BB}	x_{CB}
t = 25 °C											
0.9976	0.0010	0.0015	0.9909	0.0005	0.0085	0.0448	0.8738	0.0814	0.0823	0.4654	0.4523
0.9963	0.0009	0.0028	0.9895	0.0004	0.0101	0.0512	0.7862	0.1626	0.0881	0.3891	0.5228
0.9949	0.0008	0.0043	0.9883	0.0004	0.0113	0.0605	0.6903	0.2492	0.0985	0.3182	0.5833
0.9935	0.0007	0.0058	0.9870	0.0003	0.0128	0.0675	0.6111	0.3214	0.1125	0.2345	0.6530
0.9922	0.0006	0.0072	0.9858	0.0002	0.0141	0.0751	0.5414	0.3835	0.1352	0.1497	0.7151
t = 30 °C											
0.9973	0.0013	0.0014	0.9913	0.0006	0.0081	0.0669	0.8382	0.0949	0.1004	0.4429	0.4567
0.9960	0.0012	0.0028	0.9900	0.0005	0.0095	0.0758	0.7434	0.1808	0.1108	0.3649	0.5243
0.9949	0.0010	0.0041	0.9887	0.0004	0.0109	0.0804	0.6575	0.2622	0.1247	0.2876	0.5877
0.9936	0.0009	0.0055	0.9873	0.0003	0.0124	0.0837	0.5844	0.3319	0.1338	0.2112	0.6550
0.9926	0.0007	0.0067	0.9862	0.0002	0.0136	0.0940	0.5180	0.3880	0.1526	0.1305	0.7169
t = 35 °C											
0.9970	0.0016	0.0014	0.9917	0.0008	0.0075	0.0774	0.8143	0.1083	0.1178	0.4219	0.4602
0.9959	0.0014	0.0027	0.9905	0.0006	0.0089	0.0861	0.7218	0.1921	0.1269	0.3471	0.5260
0.9950	0.0013	0.0037	0.9893	0.0005	0.0102	0.0951	0.6373	0.2676	0.1418	0.2696	0.5886
0.9939	0.0011	0.0050	0.9879	0.0004	0.0118	0.1003	0.5672	0.3325	0.1526	0.1903	0.6571
0.9929	0.0009	0.0062	0.9866	0.0002	0.0132	0.1112	0.4927	0.3961	0.1645	0.1148	0.7207
t = 40 °C											
0.9966	0.0020	0.0013	0.9919	0.0010	0.0071	0.0964	0.7810	0.1226	0.1319	0.3982	0.4699
0.9957	0.0018	0.0025	0.9907	0.0008	0.0085	0.1003	0.6992	0.2005	0.1463	0.3224	0.5314
0.9948	0.0016	0.0037	0.9895	0.0006	0.0100	0.1141	0.6078	0.2781	0.1517	0.2480	0.6002
0.9939	0.0013	0.0048	0.9881	0.0004	0.0115	0.1181	0.5399	0.3420	0.1652	0.1690	0.6658
0.9930	0.0012	0.0059	0.9869	0.0002	0.0129	0.1250	0.4748	0.4002	0.1821	0.0921	0.7258
t = 45 °C											
0.9964	0.0024	0.0012	0.9919	0.0012	0.0070	0.1180	0.7515	0.1305	0.1519	0.3646	0.4835
0.9953	0.0022	0.0025	0.9907	0.0009	0.0084	0.1254	0.6622	0.2124	0.1590	0.2910	0.5500
0.9947	0.0019	0.0034	0.9895	0.0007	0.0097	0.1311	0.5830	0.2859	0.1715	0.2163	0.6122
0.9938	0.0017	0.0046	0.9883	0.0005	0.0112	0.1332	0.5101	0.3567	0.1861	0.1441	0.6698
0.9928	0.0014	0.0058	0.9871	0.0002	0.0127	0.1423	0.4334	0.4244	0.2006	0.0690	0.7305

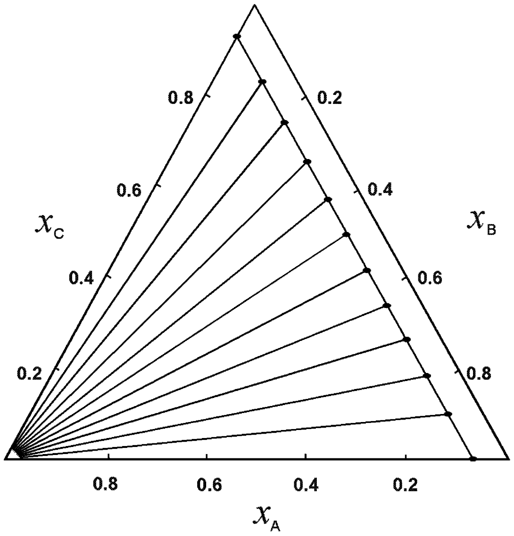

Figure 2. Ternary phase diagram for the system water (A) + benzonitrile (B) + butyl acetate (C) at 35 °C.

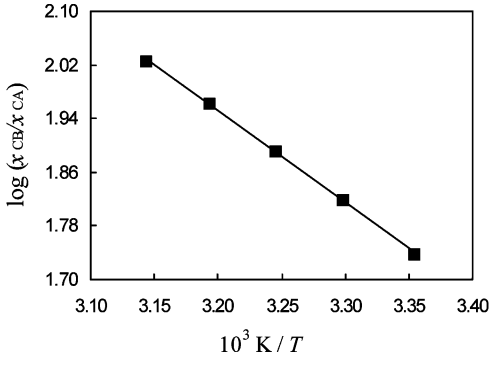

Figure 3. Temperature dependence of the logarithm of the distribution coefficient at infinite dilution, log(x_{CB}/x_{CA}), for the system water + benzonitrile + ethyl acetate.

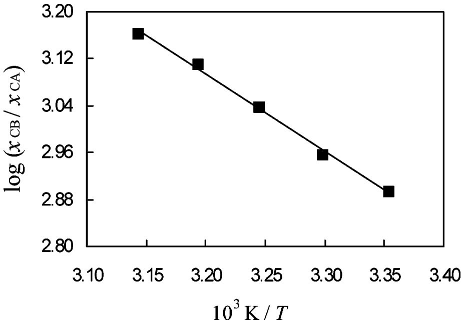

Figure 4. Temperature dependence of the logarithm of the distribution coefficient at infinite dilution, log(x_{CB}/x_{CA}), for the system water + benzonitrile + butyl acetate.

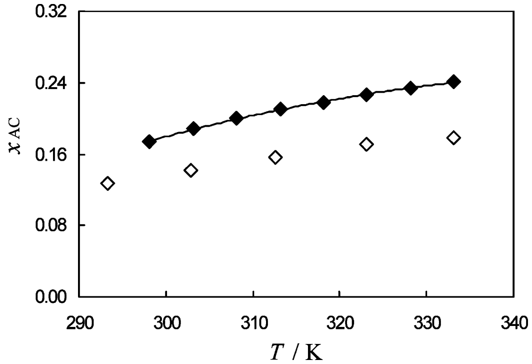

Figure 5. Solubility measurements, x_{AC}, for the binary systems water + ethyl acetate: ◆, this work; ◇, ref 8.

diagrams for both systems is shown, at 35 °C, in Figures 1 and 2. As usual, the area corresponding to the heterogeneous region diminishes with increasing temperature.

As in previous work, a plot of the logarithm of ester concentration in the water-rich phase versus the logarithm of its concentration in the benzonitrile-rich phase yields a

Table 2. Tie-Line Data for the System Water (A) + Benzonitrile (B) + Butyl Acetate (C) at Several Temperatures

water-rich phase						benzonitrile-rich phase					
x_{AA}	x_{BA}	x_{CA}	x_{AA}	x_{BA}	x_{CA}	x_{AB}	x_{BB}	x_{CB}	x_{AB}	x_{BB}	x_{CB}
					t = 25 °C						
0.9989	0.0010	0.0001	0.9990	0.0005	0.0005	0.0422	0.8795	0.0782	0.0533	0.4742	0.4724
0.9989	0.0009	0.0002	0.9990	0.0004	0.0006	0.0445	0.7890	0.1666	0.0555	0.3954	0.5491
0.9989	0.0008	0.0003	0.9990	0.0003	0.0007	0.0467	0.7012	0.2522	0.0567	0.3172	0.6261
0.9989	0.0007	0.0004	0.9990	0.0002	0.0008	0.0489	0.6299	0.3213	0.0580	0.2413	0.7008
0.9989	0.0006	0.0004	0.9990	0.0001	0.0009	0.0511	0.5503	0.3986	0.0601	0.1440	0.7959
					t = 30 °C						
0.9986	0.0013	0.0001	0.9989	0.0007	0.0005	0.0571	0.8616	0.0813	0.0625	0.4558	0.4817
0.9986	0.0012	0.0002	0.9989	0.0005	0.0006	0.0582	0.7707	0.1711	0.0636	0.3721	0.5643
0.9987	0.0010	0.0003	0.9989	0.0004	0.0007	0.0593	0.6839	0.2568	0.0647	0.2932	0.6421
0.9987	0.0009	0.0003	0.9989	0.0003	0.0008	0.0603	0.6121	0.3275	0.0658	0.2112	0.7231
0.9988	0.0008	0.0004	0.9990	0.0002	0.0009	0.0614	0.5378	0.4008	0.0669	0.1222	0.8110
					t = 35 °C						
0.9982	0.0017	0.0001	0.9987	0.0008	0.0005	0.0675	0.8344	0.0981	0.0701	0.4348	0.4951
0.9984	0.0015	0.0002	0.9988	0.0007	0.0006	0.0680	0.7491	0.1829	0.0707	0.3568	0.5725
0.9985	0.0013	0.0002	0.9988	0.0005	0.0006	0.0685	0.6682	0.2633	0.0712	0.2774	0.6514
0.9986	0.0011	0.0003	0.9989	0.0004	0.0007	0.0691	0.5919	0.3391	0.0717	0.1880	0.7403
0.9986	0.0010	0.0004	0.9989	0.0002	0.0009	0.0696	0.5145	0.4159	0.0723	0.0984	0.8294
					t = 40 °C						
0.9978	0.0021	0.0001	0.9985	0.0010	0.0005	0.0876	0.8092	0.1033	0.0833	0.4159	0.5008
0.9980	0.0019	0.0002	0.9986	0.0009	0.0005	0.0868	0.7215	0.1917	0.0822	0.3321	0.5857
0.9981	0.0017	0.0002	0.9987	0.0007	0.0006	0.0861	0.6446	0.2693	0.0812	0.2533	0.6655
0.9983	0.0014	0.0003	0.9988	0.0005	0.0007	0.0850	0.5647	0.3503	0.0804	0.1717	0.7479
0.9984	0.0012	0.0004	0.9989	0.0003	0.0008	0.0842	0.4877	0.4282	0.0793	0.0882	0.8325
					t = 45 °C						
0.9975	0.0025	0.0001	0.9983	0.0012	0.0004	0.1141	0.7697	0.1162	0.0995	0.3882	0.5123
0.9976	0.0023	0.0001	0.9985	0.0010	0.0005	0.1111	0.6965	0.1925	0.0965	0.3174	0.5861
0.9978	0.0020	0.0002	0.9986	0.0008	0.0006	0.1082	0.6180	0.2738	0.0935	0.2347	0.6717
0.9980	0.0017	0.0003	0.9987	0.0006	0.0007	0.1053	0.5478	0.3469	0.0907	0.1591	0.7502
0.9982	0.0015	0.0004	0.9988	0.0004	0.0008	0.1024	0.4673	0.4303	0.0877	0.0693	0.8430

Table 3. Solubility Data for the System Water (A) + Ethyl Acetate (C)

	water-rich phase		ethyl acetate-rich phase	
t/°C	x_{AA}	x_{CA}	x_{AC}	x_{CC}
25	0.9837	0.0163	0.1733	0.8267
30	0.9845	0.0155	0.1885	0.8115
35	0.9851	0.0149	0.1997	0.8003
40	0.9856	0.0144	0.2111	0.7889
45	0.9860	0.0140	0.2179	0.7821
50	0.9863	0.0137	0.2259	0.7741
55	0.9866	0.0134	0.2333	0.7667
60	0.9867	0.0133	0.2414	0.7586

Table 4. Solubility Data for the System Water (A) + Butyl Acetate (C)

	water-rich phase		butyl acetate-rich phase	
t/°C	x_{AA}	x_{CA}	x_{AC}	x_{CC}
25	0.9990	0.0010	0.0644	0.9356
30	0.9990	0.0010	0.0680	0.9320
35	0.9990	0.0010	0.0729	0.9271
40	0.9991	0.0009	0.0784	0.9216
45	0.9991	0.0009	0.0848	0.9152
50	0.9991	0.0009	0.0927	0.9073
55	0.9991	0.0009	0.1004	0.8996
60	0.9991	0.0009	0.1073	0.8927

straight line with a slope close to 1, a fact that indicates that no association reactions involving the ester occur.[7]

The enthalpy of transfer of the ester from the benzonitrile-rich phase to the water-rich phase was obtained, as in previous work, by plotting the logarithm of the distribution coefficient, $m_c = x_{C,B}/x_{C,A}$, at infinite dilution against T^{-1} as shown in Figures 3 and 4. From these plots, we find that the transfer of both esters has almost no thermal effect because ΔH_{tr} is -26.2 J mol^{-1} in the case of ethyl acetate and -25.2 J mol^{-1} for butyl acetate.

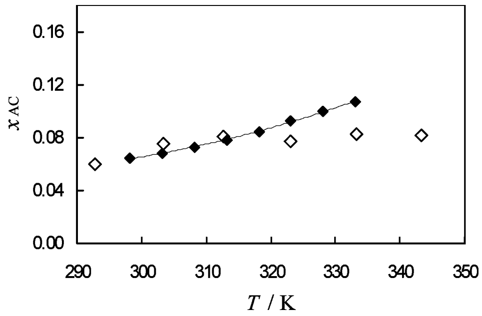

Figure 6. Solubility measurements, x_{AC}, for the binary systems water + butyl acetate: ◆, this work; ◇, ref 8.

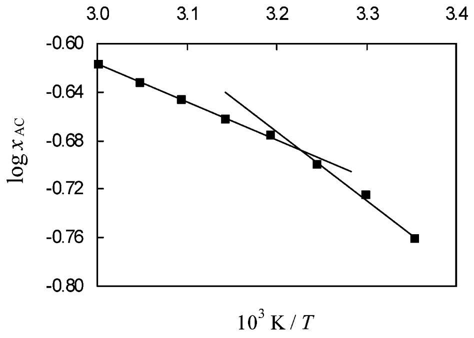

Figure 7. Temperature dependence of water solubility in ethyl acetate.

Solubility measurements for the binary systems water + ethyl acetate or + butyl acetate were carried out in the temperature range of 25 °C to 60 °C with the same experimental technique. The obtained data are reported in Tables 3 and 4. Here $x_{A,C}$ and $x_{C,A}$ are, respectively, the molar fraction of water in the organic phase and the molar fraction of the ester in the aqueous phase.

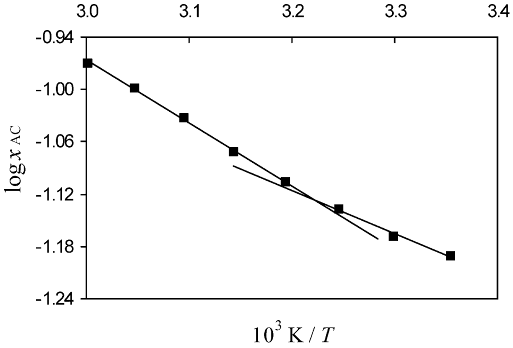

Figure 8. Temperature dependence of water solubility in butyl acetate.

A comparison of these data with previously published values[8] shows very good agreement for the water-rich phase. However, there are significant differences for the organic-rich phase, as shown in Figures 5 and 6. This is probably due to the larger uncertainty of their GC analysis.

Finally, if $\log x_{AC}$ is plotted as a function of T^{-1} then the lines shown in Figures 7 and 8 are obtained. It is interesting that a change in slope is observed for both cases at 35 °C to 40 °C. This change in the solution behavior can be assigned, in an approximation based on van Laar's model, to a change in the entropy of solution of water in the esters. However, this point should be studied further.

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