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Solubility of Benzimidazoles in Alcohols

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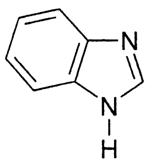
The solid−liquid equilibrium (SLE) has been measured from 270 K to 445 K for 10 binary mixtures of benzimidazoles (benzimidazole and 2-methylbenzimidazole) with alcohols (1-propanol, 1-butanol, 2-butanol, 2-methyl-2-propanol, 1-hexanol) using a dynamic method. The melting point, enthalpy of fusion, and heat capacity change at the melting temperature were determined by differential scanning calorimetry (DSC). The solubility of benzimidazoles in alcohols (C_3−C_6) is higher than in water and in 1-octanol and generally decreases with an increase of the alkyl chain length of the alcohol. The intermolecular solute−solvent interaction is higher for the 1-alcohol than for the secondary or tertiary alcohol. The solubility of 2-methylbenzimidazole in alcohols (C_3−C_6) is higher than that of benzimidazole. Experimental results of solubility were correlated by means of the Wilson, UNIQUAC ASM, and NRTL 1 equations utilizing parameters derived from SLE results. The existence of a solid−solid first-order phase transition in benzimidazole and 2-methylbenzimidazole has been observed in the DSC measurements and has been taken into consideration in the solubility calculation. The best correlation of the solubility data has been obtained by the NRTL 1 equation.

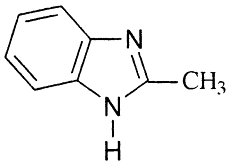
Introduction

The molecular structures of the benzimidazoles under study are as follows:

Benzimidazole (BI)



2-Methylbenzimidazole (2MBI)



These two substances have a large aromatic group substituted to the imidazole ring causing hydrophobic hydration effects, manifesting in an enhancement of the water, or an alcohol structure. On the other hand, the existence of two hydrophilic groups of nitrogen at the 1 + 3 position in the imidazole molecules could imply specific interactions between them, as well as with bulk-alcohol structure, strongly changing the solubility of the solutes under investigation. Thus, benzimidazoles were chosen not only because of the large hydrophobic groups but also for the known specific interactions of nitrogen atoms, or the hydrogen atom with solvent, an alcohol molecules. The structure of the solution and the molecular rearrangements and the variation in the solubility depend on the possibility of hydrogen bond formation between the imidazole molecules N−H···N and between the imidazole and an alcohol molecule. The hydrogen bonds O−H···N and N−H···O are responsible for structures as building blocks of salts of imidazole with mono-, di-, or tetracarboxylic acids.[1] Most important, imidazolium ionic liquids are polymeric supramolecules of weak interactions. These ionic liquids form aggregates (through hydrogen bonds) even in solution with polar solvents, which is widely used in chemical processes and in pharmacology. The tendency of complex formation was helpful for developing several ruthenium(III) complexes which are under clinical examination in cancer therapy.[2,3]

We have begun systematic investigations into the physicochemical properties and phase equilibria of simple imidazole and benzimidazole and their derivatives.[4−8] The purpose of these measurements was to get basic information about the interaction of the imidazoles with water and different solvents, having in mind a new class of low-melting *N*,*N*′-dialkylimidazolium salts, which are presently known as some of the most inert and least nucleophilic anions. The packing inefficiency of the *N*,*N*′-dialkylimidazolium salts and the asymmetry of the cation are the major reasons for their low melting temperatures.[9] The other useful properties of these salts are negligible vapor pressure, high electrical conductivity, wide electrochemical window, tolerance to strong acids, and excellent thermal and chemical stability. Ionic liquids are excellent solvents for a broad range of polar and nonpolar organic compounds. Their unique properties have stimulated intense interest commercially in their use as environmentally benign solvents, that could replace many volatile organic compounds currently in use as solvents for chemical reactions. Ionic liquids exhibit some unusual mixture properties. Our first measurements of the phase equilibria of 1-alkyl-3-methylimidazolium hexafluorophosphate or chloride were presented previously.[10−13]

The purpose of this paper is to report the examination of solid−liquid equilibria in binary mixtures of benzimidazoles (benzimidazole (BI) and 2-methylbenzimidazole (2MBI)) with alcohols (1-propanol, 1-butanol, 2-butanol, 2-methyl-2-propanol, 1-hexanol) using a dynamic method.

The present data will be useful for the testing of new theories of liquid mixtures to predict the thermodynamic properties of mixtures containing imidazoles and ionic liquids.

Experimental Section

The origins of the chemicals (Chemical Abstracts registry numbers are in parentheses) and their mass percent

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Table 1. Physical Constants of Pure Compounds: T_m, Melting Temperatures; ΔH_m, Molar Enthalpy of Fusion; ΔCp_m, Heat Capacity Change at the Melting Temperature; and V_m(298.15 K), Molar Volume

component	T_{m1}/K	T_{tr1}/K	ΔH_{m1}/kJ·mol^{-1}	ΔH_{tr1}/kJ·mol^{-1}	ΔCp_{m1}/J·K-1·mol^{-1}	V_m(298.15 K)^a/cm^3·mol^{-1}
benzimidazole^b	445.51	384.43	20.472	0.710	49.09	89.2
2-methylbenzimidazole^b	451.43	383.93	20.486	0.586	50.58	103.7

[a] Calculated with the group contribution method from ref 14. [b] Published previously in ref 5.

Table 2. Experimental Solid−Liquid Equilibrium Temperatures (T, Phases α_1, α_2, and β_1, Respectively) for Systems of {Benzimidazole (1) + an Alcohol (2)}^{a}

x_1	T_{α_1}, T_{α_2}, or T_{β_1}/K	γ_1	x_1	T_{α_1}, T_{α_2}, or T_{β_1}/K	γ_1	x_1	T_{α_1}, T_{α_2}, or T_{β_1}/K	γ_1	x_1	T_{α_1}, T_{α_2}, or T_{β_1}/K	γ_1
1-Propanol											
0.1055	287.56 (β_1)	2.11	0.1502	311.26 (β_1)	2.22	0.2090	333.81 (β_1)	2.35	0.2831	357.17 (β_1)	2.47
0.1118	291.40 (β_1)	2.13	0.1666	317.72 (β_1)	2.26	0.2245	339.21 (β_1)	2.38	0.2979	359.94 (β_1)	2.49
0.1216	296.91 (β_1)	2.15	0.1781	323.18 (β_1)	2.28	0.2390	345.93 (β_1)	2.40	1.0000	445.51 (α_1)	1.00
0.1290	300.82 (β_1)	2.17	0.1808	326.96 (β_1)	2.29	0.2565	350.27 (β_1)	2.43			
0.1355	304.37 (β_1)	2.18	0.1952	329.57 (β_1)	2.32	0.2640	351.94 (β_1)	2.44			
0.1431	310.23 (β_1)	2.20	0.1974	330.88 (β_1)	2.32	0.2799	355.41 (β_1)	2.47			
1-Butanol											
0.0919	286.60 (β_1)	2.28	0.1277	308.83 (β_1)	2.38	0.1734	329.99 (β_1)	2.52	0.2308	350.36 (β_1)	2.68
0.0941	288.97 (β_1)	2.27	0.1298	311.72 (β_1)	2.39	0.1820	333.72 (β_1)	2.54	0.2406	354.07 (β_1)	2.70
0.0998	294.57 (β_1)	2.31	0.1391	314.50 (β_1)	2.42	0.1894	337.27 (β_1)	2.56	0.2502	355.87 (β_1)	2.73
0.1057	294.84 (β_1)	2.31	0.1500	318.90 (β_1)	2.42	0.2044	342.17 (β_1)	2.61	0.2566	360.22 (β_1)	2.74
0.1075	297.96 (β_1)	2.32	0.1522	321.58 (β_1)	2.45	0.2114	344.16 (β_1)	2.62	1.0000	445.51 (α_1)	1.00
0.1172	302.38 (β_1)	2.35	0.1648	326.30 (β_1)	2.49	0.2162	344.14 (β_1)	2.64			
0.1180	303.47 (β_1)	2.35	0.1689	327.43 (β_1)	2.50	0.2238	347.72 (β_1)	2.66			
2-Butanol											
0.0902	284.37 (β_1)	2.24	0.1250	308.51 (β_1)	2.34	0.1659	326.49 (β_1)	2.50	0.2345	351.61 (β_1)	2.66
0.0963	289.22 (β_1)	2.26	0.1321	310.85 (β_1)	2.37	0.1732	328.70 (β_1)	2.49	0.2480	352.49 (β_1)	2.70
0.0998	291.73 (β_1)	2.27	0.1360	311.25 (β_1)	2.38	0.1759	331.07 (β_1)	2.50	0.2617	358.89 (β_1)	2.73
0.1100	297.98 (β_1)	2.30	0.1373	312.72 (β_1)	2.38	0.1924	335.54 (β_1)	2.54	0.2750	362.64 (β_1)	2.76
0.1142	300.94 (β_1)	2.31	0.1401	314.24 (β_1)	2.39	0.2042	340.21 (β_1)	2.58	0.2817	362.90 (β_1)	2.78
0.1191	302.41 (β_1)	2.33	0.1453	317.35 (β_1)	2.41	0.2156	342.69 (β_1)	2.61	0.2884	363.61 (β_1)	2.79
0.1206	302.84 (β_1)	2.33	0.1538	321.55 (β_1)	2.43	0.2242	347.17 (β_1)	2.64	1.0000	445.51 (α_1)	1.00
2-Methyl-2-propanol											
0.0000	297.99 (α_2)		0.0682	290.99 (α_2)		0.1177	297.56 (β_1)	2.18	0.1665	319.33 (β_1)	2.36
0.0050	297.31 (α_2)		0.0772	289.72 (α_2)		0.1282	302.82 (β_1)	2.22	0.1783	329.86 (β_1)	2.41
0.0087	296.95 (α_2)		0.0860	287.79 (α_2)		0.1304	303.77 (β_1)	2.22	0.1919	334.69 (β_1)	2.46
0.0191	296.46 (α_2)		0.0947	286.60 (β_1)	2.09	0.1389	307.41 (β_1)	2.26	0.2100	347.73 (β_1)	2.53
0.0314	295.55 (α_2)		0.1006	289.55 (β_1)	2.11	0.1487	313.77 (β_1)	2.29	0.2209	350.44 (β_1)	2.57
0.0508	293.84 (α_2)		0.1057	293.83 (β_1)	2.13	0.1578	314.79 (β_1)	2.33	0.2246	355.08 (β_1)	2.59
0.0595	292.49 (α_2)		0.1095	295.61 (β_1)	2.15	0.1656	325.94 (β_1)	2.36	1.0000	445.51 (α_1)	1.00
1-Hexanol											
0.0962	273.59 (β_1)	0.40	0.1373	308.12 (β_1)	0.83	0.1864	329.68 (β_1)	0.99	0.2429	348.97 (β_1)	1.13
0.0992	281.15 (β_1)	0.54	0.1490	313.53 (β_1)	0.87	0.1934	332.19 (β_1)	1.00	0.2638	355.75 (β_1)	1.21
0.1058	288.15 (β_1)	0.64	0.1542	315.01 (β_1)	0.85	0.1989	333.55 (β_1)	1.00	0.2781	360.80 (β_1)	1.28
0.1129	293.62 (β_1)	0.70	0.1573	316.84 (β_1)	0.88	0.2062	337.85 (β_1)	1.08	0.2916	363.81 (β_1)	1.28
0.1199	296.90 (β_1)	0.70	0.1693	322.69 (β_1)	0.94	0.2139	342.46 (β_1)	1.19	1.0000	445.51 (α_1)	1.00
0.1283	301.82 (β_1)	0.75	0.1740	324.23 (β_1)	0.94	0.2320	346.11 (β_1)	1.13			

[a] γ_1, experimental activity coefficient of the solute.

purities are as follows: 1-propanol (71-23-8, POCH, Gliwice, >99%), 1-butanol (71-36-3, POCH, Gliwice, HPLC grade), 2-butanol (78-92-2, Ubichem Limited Angleterre, >99%), 2-methyl-2-propanol (3972-25-6, Aldrich, 99.5+%), 1-hexanol (111-27-3 Reachim, 99%), benzimidazole (51-17-2, Koch-Light Laboratory, 98%), and 2-methylbenzimidazole (615-15-6, Koch Light Laboratory, 98%). Solutes before use were dried for 24 h in a vacuum at the temperature 330 K. All solvents were fractionally distilled over different drying reagents to a mass fraction purity of better than 99.8%. Liquids were stored over freshly activated molecular sieves of type 4A (Union Carbide). All compounds were checked by gas−liquid chromatography (GLC) analysis, and no significant impurities were found. Analysis, using the Karl Fisher technique, showed that the water contamination in alcohols was less than 0.02 mass %. Physical properties of pure benzimidazoles are collected in Table 1. Molar enthalpies of fusion have been measured by the differential scanning microcalorimeter Perkin-Elmer Pyris 1 as described before.[5] The values of the molar heat capacities during the melting process, ΔCp_m, were obtained from heat capacity measurements carried out from at least 50 K above melting temperatures with thorough care to eliminate the premelting range. The Micro Cal ITC calorimeter was used from 300 K to 350 K and Microcalorimeter TG-DSC 111 for the higher temperatures for the ΔCp_m measurements.[5] The calorimetric accuracy was ±5 J·K^{-1}·mol^{-1}.

Solid−liquid equilibrium (SLE) temperatures were determined using a dynamic method described in detail previously.[15] Mixtures were heated very slowly (at less than 2 K·h^{-1} near the equilibrium temperature) with continuous stirring inside a Pyrex glass cell, placed in a thermostat. The crystal disappearance temperatures, detected visually, were measured with an electronic thermometer P 500 (DOSTMANN electronic GmbH) with the probe totally

Table 3. Experimental Solid−Liquid Equilibrium Temperatures (T, Phases α_1, α_2, and β_1, Respectively) for Systems of {2-Methylbenzimidazole (1) + an Alcohol (2)}[a]

x_1	T_{α_1}, T_{α_2}, or T_{β_1}/K	γ_1	x_1	T_{α_1}, T_{α_2}, or T_{β_1}/K	γ_1	x_1	T_{α_1}, T_{α_2}, or T_{β_1}/K	γ_1	x_1	T_{α_1}, T_{α_2}, or T_{β_1}/K	γ_1
1-Propanol											
0.1059	277.43 (β_1)	0.40	0.1644	305.99 (β_1)	0.49	0.2185	326.25 (β_1)	0.57	0.3222	358.03 (β_1)	0.74
0.1189	282.77 (β_1)	0.39	0.1706	308.52 (β_1)	0.52	0.2258	327.65 (β_1)	0.55	0.3466	363.76 (β_1)	0.77
0.1297	289.45 (β_1)	0.42	0.1826	313.71 (β_1)	0.50	0.2476	333.02 (β_1)	0.55	0.3593	366.87 (β_1)	0.79
0.1398	294.09 (β_1)	0.43	0.1873	314.19 (β_1)	0.50	0.2590	337.14 (β_1)	0.58	1.0000	451.43 (α_1)	1.00
0.1514	300.91 (β_1)	0.48	0.1941	317.88 (β_1)	0.54	0.2710	342.15 (β_1)	0.63			
0.1581	307.31 (β_1)	0.56	0.1998	318.98 (β_1)	0.52	0.2859	346.78 (β_1)	0.65			
0.1585	305.20 (β_1)	0.52	0.2141	323.92 (β_1)	0.54	0.3009	352.63 (β_1)	0.72			
1-Butanol											
0.1130	278.04 (β_1)	0.35	0.1624	305.50 (β_1)	0.49	0.2212	330.66 (β_1)	0.65	0.2981	356.64 (β_1)	0.85
0.1225	282.73 (β_1)	0.36	0.1689	309.46 (β_1)	0.53	0.2353	336.73 (β_1)	0.71	0.3198	361.42 (β_1)	0.85
0.1253	286.75 (β_1)	0.41	0.1745	314.63 (β_1)	0.60	0.2438	339.56 (β_1)	0.72	1.0000	451.43 (α_1)	1.00
0.1359	291.07 (β_1)	0.41	0.1891	316.53 (β_1)	0.54	0.2569	342.96 (β_1)	0.73			
0.1481	297.12 (β_1)	0.43	0.1947	320.58 (β_1)	0.59	0.2687	347.10 (β_1)	0.76			
0.1569	302.01 (β_1)	0.46	0.2087	325.30 (β_1)	0.61	0.2872	352.10 (β_1)	0.79			
2-Butanol											
0.1054	283.43 (β_1)	2.04	0.1456	308.47 (β_1)	2.15	0.2016	330.66 (β_1)	2.31	0.2610	348.85 (β_1)	2.45
0.1106	288.44 (β_1)	2.05	0.1543	311.98 (β_1)	2.18	0.2173	334.16 (β_1)	2.35	0.2732	352.64 (β_1)	2.48
0.1180	292.13 (β_1)	2.07	0.1625	315.04 (β_1)	2.20	0.2276	337.02 (β_1)	2.37	0.2907	358.32 (β_1)	2.51
0.1279	297.42 (β_1)	2.10	0.1779	320.37 (β_1)	2.25	0.2362	340.57 (β_1)	2.40	1.0000	451.43 (α_1)	1.00
0.1394	303.65 (β_1)	2.14	0.1898	325.74 (β_1)	2.28	0.2474	344.60 (β_1)	2.42			
2-Methyl-2-propanol											
0.0000	297.99 (α_2)		0.0576	289.84 (α_2)		0.1116	294.21 (β_1)	2.17	0.1778	325.81 (β_1)	2.42
0.0018	297.60 (α_2)		0.0594	290.68 (α_2)		0.1191	294.76 (β_1)	2.2	0.1994	332.38 (β_1)	2.20
0.0055	297.00 (α_2)		0.0667	289.80 (α_2)		0.1245	296.88 (β_1)	2.22	0.2074	335.43 (β_1)	2.53
0.0145	296.00 (α_2)		0.0751	288.83 (α_2)		0.1292	300.99 (β_1)	2.23	0.2195	339.46 (β_1)	2.57
0.0217	295.36 (α_2)		0.0811	287.08 (α_2)		0.1324	301.91 (β_1)	2.25	0.2305	344.49 (β_1)	2.61
0.0297	294.91 (α_2)		0.0887	283.83 (α_2)		0.1410	306.76 (β_1)	2.28	0.2446	349.46 (β_1)	2.65
0.0339	294.50 (α_2)		0.0967	281.71 (β_1)	2.11	0.1470	308.77 (β_1)	2.30	0.2490	352.95 (β_1)	2.67
0.0376	292.99 (α_2)		0.1022	284.86 (β_1)	2.13	0.1536	312.72 (β_1)	2.33	1.0000	451.43 (α_1)	1.00
0.0428	293.00 (α_2)		0.1071	288.25 (β_1)	2.15	0.1643	319.28 (β_1)	2.37			
1-Hexanol											
0.1258	273.86 (β_1)	0.23	0.1424	289.63 (β_1)	0.43	0.1980	319.12 (β_1)	0.54	0.2856	354.70 (β_1)	0.87
0.1270	277.16 (β_1)	0.26	0.1465	291.13 (β_1)	0.34	0.2081	321.72 (β_1)	0.53	0.2972	356.85 (β_1)	0.86
0.1304	280.13 (β_1)	0.28	0.1517	293.96 (β_1)	0.36	0.2166	325.18 (β_1)	0.55	0.3091	361.23 (β_1)	0.92
0.1334	283.14 (β_1)	0.30	0.1558	294.71 (β_1)	0.35	0.2189	326.44 (β_1)	0.57	0.3240	366.25 (β_1)	0.98
0.1343	283.87 (β_1)	0.31	0.1635	298.98 (β_1)	0.37	0.2353	332.42 (β_1)	0.60	0.3394	368.67 (β_1)	0.99
0.1353	284.74 (β_1)	0.31	0.1694	302.95 (β_1)	0.40	0.2500	340.48 (β_1)	0.71	1.0000	451.43 (α_1)	1.00
0.1379	286.04 (β_1)	0.32	0.1781	307.44 (β_1)	0.43	0.2657	345.49 (β_1)	0.74			
0.1390	286.62 (β_1)	0.32	0.1889	313.58 (β_1)	0.48	0.2767	351.01 (β_1)	0.82			

[a] γ_1, experimental activity coefficient of the solute.

immersed in the thermostating liquid. The thermometer was calibrated on the basis of the ITS-90 scale of temperature. The accuracy of temperature measurements was ±0.01 K. Mixtures were prepared by weighing the pure components to within 2×10^{-4} g. The error in the mole fraction did not exceed $\delta x_1 = 0.0002$.

Results and Discussion

Tables 2 and 3 list the direct experimental results of the SLE temperatures, T versus x_1, the mole fraction of the benzimidazoles, and γ_1, the experimental activity coefficients in saturated solution for the investigated systems. The experimental values of the eutectic temperature (T_e) and eutectic composition, $x_{1,e}$ (determined graphically), observed in benzimidazole + 2-methyl-2-propanol or 2-methylbenzimidazole + 2-methyl-2-propanol binary mixtures are collected in Table 4. The solubilities of BI or 2MBI (1) + 1-butanol, 2-butanol, 2-methyl-2-propanol, or 1-hexanol (2) are presented in Figures 1 and 2, respectively.

Experimental phase diagrams of SLE investigated in this work are characterized mainly by the following:

(i) The solubility is very close to the ideal solubility. Slightly positive deviations from ideality were found for the liquidus curve of BI in most of the mixtures, and thus the solubility was lower than the ideal one ($\gamma_1 > 1$). Slightly negative deviations from ideality were found for 2MBI ($\gamma_1 < 1$) in primary alcohols (see the values of the activity coefficients in Tables 2 and 3; benzimidazoles have high temperatures and enthalpies of melting, and they are sparingly soluble in alcohols in comparison with simple imidazoles).[4]

Table 4. Eutectic Temperatures, $T_{1,e}$, and Composition, $x_{1,e}$, Detected Graphically for Systems of {Benzimidazole or 2-Methylbenzimidazole (1) + 2-Methyl-2-propanol(2)}

system	$x_{1,e}$	T_{1e} /K
benzimidazole + 2-methyl-2-propanol	0.09 ± 0.01	286.60 ± 0.1
2-methylbenzimidazole + 2-methyl-2-propanol	0.10 ± 0.01	281.71 ± 0.1

(ii) The solubility of benzimidazoles in alcohols decreases with an increase of the alkyl chain length of an alcohol.

(iii) The liquidus curves of the primary, secondary, and tertiary alcohols exhibit similar shapes. The differences in solubilities are small, and the solubility increases in the order 1-butanol > 2-butanol > 2-methyl-2-propanol (see Figure 1).

(iv) The solubility of 2MBI is better than that of BI in all alcohols even though the temperature and the enthalpy

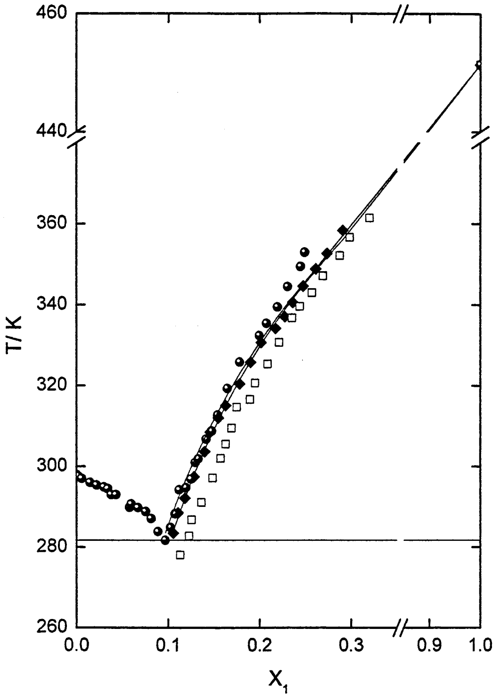

Figure 1. Solid−liquid equilibrium diagram for binary mixtures of 2-methylbenzimidazole (1) + □, 1-butanol; or ◆, 2-butanol; or ●, 2-methyl-2-propanol (2). Solid lines, calculated by the UNIQUAC ASM equation.

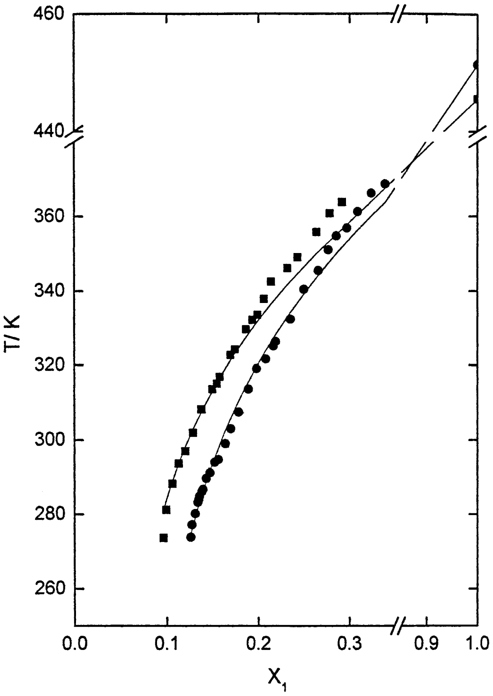

Figure 2. Solid−liquid equilibrium diagram for binary mixtures of ■, benzimidazole; or ●, 2-methylbenzimidazole (1) + 1-hexanol (2). Solid lines, calculated by the NRTL 1 equation.

of melting are higher. The temperature and enthalpy of the solid−solid phase transition are similar for these two compounds, and thus there is no doubt that the reason for their different solubilities is a result of solute−solvent interaction.

This is the evidence that the interaction of the hydrogen atom of 2MBI with the OH-group of alcohols is stronger than for the BI molecules. The inductive effect of the substituted methyl group on the side of the imidazole ring

Table 5. Molar Volume, V_m, and Association Parameters for Alcohols

alcohol	V_m(298.15 K) $cm^3 \cdot mol^{-1}$ [a]	$-\Delta H$ $kJ \cdot mol^{-1}$	K(298.15 K)
1-propanol	72.7	25.1[b]	197[b]
1-butanol	92.0	25.1[b]	175[b]
2-butanol	92.4	25.1	150
2-methyl-2-propanol	94.9	25.1	110
1-hexanol	125.3	25.1[c]	120[c]

[a] From ref 22. [b] From ref 23. [c] From ref 24.

is supposed to result in an enhancement of A−B interaction.

If a solid−solid phase transition occurs before fusion, the solubility of a solid 1 in a liquid may be expressed in a very general manner by eq 1. The solubility equation for temperatures below that of the phase transition must include the effect of the transition. The result for the first-order transition is

$$-\ln x_1 = \frac{\Delta H_{m1}}{R}\left(\frac{1}{T}-\frac{1}{T_{m1}}\right) + \frac{\Delta H_{tr1}}{R}\left(\frac{1}{T}-\frac{1}{T_{tr1}}\right) - \frac{\Delta Cp_{m1}}{R}\left(\ln\frac{T}{T_{m1}} + \frac{T_{m1}}{T} - 1\right) + \ln \gamma_1 \quad (1)$$

where x_1, γ_1, ΔH_{m1}, ΔCp_{m1}, $T_{m1,}$ T, ΔH_{tr1}, and T_{tr1} stand for mole fraction, activity coefficient, enthalpy of fusion, difference in solute heat capacity between the solid and liquid at the melting point, melting point of the solute (1), equilibrium temperature, enthalpy of the solid−solid phase transition, and transition temperature, respectively. The existence of the solid−solid phase transition was observed for both solutes under study and was observed previously only for 2-methyl-1*H*-imidazole.[4]

In this study, three methods are used to derive the solute activity coefficients γ_1 from the so-called correlation equations that describe the Gibbs excess energy, (G^E): the Wilson,[16] UNIQUAC ASM,[17] and NRTL 1.[18] The exact mathematical forms of the equations have been presented in our previous paper.[19]

The parameters of the equations were found by an optimization technique using Marquardt's maximum neighborhood method of minimization:[20]

$$\Omega = \sum_{i=1}^{n}[(T_i)^{exp} - (T_i(x_{1i}P_1,P_2))^{cal}]^2 \quad (2)$$

where Ω is the objective function, $(T_i)^{exp}$ denotes the experimental temperature of the *i*th point for a given concentration x_{1i}, and $(T_i)^{cal}$ is the calculated temperature for the given concentration x_{1i} and parameters P_1 and P_2, obtained by solving the nonlinear equation (eqs 1 and 2), according to the assumed model. The root-mean-square deviation of temperature (σ_T defined by eq 3) was used as a measure of the goodness of the solubility correlation:

$$\sigma_\gamma = \left(\sum_{i=1}^{n}\frac{((T_i)^{exp} - (T_i)^{cal})^2}{n-2}\right)^{1/2} \quad (3)$$

where n is the number of experimental points (including the melting point) and 2 is the number of adjustable parameters.

The pure-component structural parameters r (volume parameter) and q (surface parameter) in the UNIQUAC

Table 6. Correlation of the Solubility Data, SLE, of {Imidazole (1) + an Alcohol (2)} by Means of the Wilson, UNIQUAC ASM, and NRTL 1 Equations: Values of Parameters and Measures of Deviations

	parameters			deviations		
	Wilson $g_{12}-g_{22}$ $g_{21}-g_{11}$	UNIQUAC ASM Δu_{12} Δu_{21}	NRTL 1[a] Δg_{12} Δg_{21}	Wilson σ_T[b]	UNIQUAC ASM σ_T[b]	NRTL σ_T[b]
alcohol	$J \cdot mol^{-1}$	$J \cdot mol^{-1}$	$J \cdot mol^{-1}$	K	K	K
		Benzimidazole				
1-propanol	−3 301.77	3 117.43	−502.01	0.93	1.01	0.92
	7 008.31	−3 341.31	−2 990.03			
1-butanol	−2 556.20	3 613.67	−2 143.49	0.91	1.13	0.99
	120 555.0	−3 041.54	−297.11			
2-butanol	−2 553.88	−1 025.18	−2 073.05	0.97	0.92	0.92
	11 198.48	−59.77	−419.14			
2-methyl-2-propanol	−2 620.31	5 292.05	−3 501.36	4.22	4.19	4.10
	87 506.68	−3 362.82	1 487.35			
1-hexanol	59 614.71	−2 019.31	−4 296.26	3.84	1.45	1.49
	−3 759.30	1 953.61	2 280.45			
		2-Methylbenzimidazole				
1-propanol	−201.53	1 310.35	2 189.62	1.56	2.76	1.79
	−587.55	−2 784.43	−6 146.67			
1-butanol	66 115	−311.32	−977.35	1.63	1.08	1.09
	−2 924.33	−1 331.48	−2 890.99			
2-butanol	4 411.51	731.95	302.50	1.37	0.93	0.92
	−2 379.71	−1 988.66	−3 608.69			
2-methyl-2-propanol	3 906.29	−578.29	−1 340.57	2.97	1.50	1.51
	−2 251.18	−739.99	−1 788.39			
1-hexanol	8 365.3	−1 622.80	−54 435.19	2.75	1.64	1.19
	−3 788.00	642.36	−98.32			

[a] Calculated with the third nonrandomness parameter $\alpha = 0.3$. [b] According to eq 3 in the text.

ASM and NRTL1 equations were obtained by means of the following simple relationships:[21]

$$R_i = 0.029281 V_m \tag{4}$$

$$q_i = \frac{(Z-2)r_i}{Z} + \frac{2(1-l_i)}{Z} \tag{5}$$

where V_m is the molar volume of pure component i at 298.15 K, Z is the coordination number, assumed to be equal to 10, and l_i is the bulk factor; it was assumed that $l_i = 1$. The calculations with the UNIQUAC ASM and NRTL 1 models were carried out by the use of the data set of association for alcohols presented in Table 5. The temperature dependence of association constants was calculated from the van't Hoff relation assuming the enthalpy of hydrogen-bond formation to be temperature independent. The Kretschmer−Wiebe model of association for the development of two adjustable parameters was used. In this work, parameter α_{12}, a constant of proportionality similar to the nonrandomness constant of the NRTL 1 equation ($\alpha_{12} = \alpha_{21} = 0.3$), was taken into account in calculations.

Table 6 lists the results of fitting the solubility curves by the three equations used: Wilson, UNIQUAC ASM, and NRTL 1.

For the 10 systems presented in this work, the best description of the solid−liquid equilibrium of benzimidazole in aliphatic alcohols (C_3−C_6) was given by the two-parameter NRTL1 equation with the average standard deviation $\sigma_T = 1.49$ K. The results of correlations by the UNIQUAC ASM present slightly worse deviations, $\sigma_T = 1.66$ K. The average standard mean deviation obtained by the Wilson equation was $\sigma_T = 2.14$ K.

Conclusions

The solubility of BI and 2MBI in alcohols decreases with an increase of the alkyl chain length of an alcohol. Simple imidazoles were more readily soluble in alcohols and water than benzimidazoles.[4,5] Primary alcohols were better solvents than secondary or tertiary alcohols. The OH− group of the primary alcohol was more attainable in the solute−solvent interaction and the creation of polymeric supramolecules in the solution. The correlation of the experimental liquidus curves is better with the models taking into account the association of the alcohols.

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