Solubility of Imidazoles, Benzimidazoles, and Phenylimidazoles in Dichloromethane, 1-Chlorobutane, Toluene, and 2-Nitrotoluene

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Solubilities of seven imidazoles (1*H*-imidazole, 2-methyl-1*H*-imidazole, benzimidazole, 2-methylbenzimidazole, 2-phenylimidazole, 4,5-diphenylimidazole, and 2,4,5-triphenylimidazole) in organic solvents (dichloromethane, 1-chlorobutane, toluene, and 2-nitrotoluene) have been measured using a synthetic method and liquid chromatography. The interactions of the imidazoles, benzimidazoles, or phenylimidazoles with different solvents are discussed. The solubilities of these imidazoles in chloroalkanes were very low. In all solvents studied, the solubility of phenylmidazoles was significantly lower than the solubility of 1*H*-imidazole or benzimidazoles. Experimental results of solubility were correlated by means of the Wilson, UNIQUAC, and NRTL equations utilizing parameters derived from solid−liquid equilibria results. The existence of a solid−solid first-order phase transition in the solute has been taken into consideration in the solubility calculation. The best correlation of the solubility data was obtained by the Wilson equation with the average root-mean-square deviation σ_T equal to 3.2 K.

Introduction

We have begun systematic investigations into the physicochemical properties and phase equilibria of systems with simple imidazoles, benzimidazoles, and phenylimidazoles.[1−8] The purpose of these measurements was to obtain information about the interaction of imidazoles, benzimidazoles, and phenylimidazoles with water and different organic solvents—alcohols, ethers, and ketones—having in mind a new class of low-melting *N*,*N*-dialkylimidazolium salts, which are presently known as some of the most popular new solvents for organic synthesis, extraction, and electrochemistry.[9−13] They are generally salts based on a substituted imidazolium or pyridinium cation and an inorganic anion such as halide or $[AlCl_4]^-$ or $[BF_4]^-$ or $[PF_6]^-$ and are often liquid at room temperature. Room-temperature ionic liquids (ILs) are being investigated as more clean replacements for volatile organic solvents. A review of recent applications of ILs has been presented along with some results of measurements of liquid−liquid equilibria and partition coefficients with alcohols.[14] The solid−liquid equilibria of a (1-decyl or 1-dodecyl-3-methylimidazolium chloride + an alcohol) binary mixture were measured and discussed concerning two solid−solid phase transitions on a liquidus curve.[15,16] The solubility of 1-ethyl-3-methylimidazolium hexafluorophosphate, [emim][PF_6], in aromatic hydrocarbons (benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene, and *p*-xylene)[17] and in alcohols was already presented by us.[18] Also, the solubilities of 1-butyl-3-methylimidazolium hexafluorophosphate, [bmim][PF_6], in the same aromatic hydrocarbons, in *n*-alkanes (pentane, hexane, heptane, and octane), and in cyclohydrocarbons (cyclopentane and cyclohexane) have been measured by us previously.[17]

The purpose of our measurements was to get basic information on the interaction of imidazoles or benzimidazoles or phenylimidazoles with very polar and interacting solvents. The packing inefficiency of the imidazolium ring and *N*,*N*-dialkylimidazolium salts and the asymmetry of the salts' cations are the major reasons for the salts' low melting temperatures[19] and the net of the hydrogen bonded structure in the liquid and solid phases.[20]

Thus, the use of imidazoles and their derivatives in chemical processes is becoming increasingly important. Their potential for hydrogen bond formation is also widely used in pharmaceuticals. Several ruthenium(III) complexes have been evaluated and used extensively in cancer therapy treatment.[21,22] Additionally, 1*H*-imidazole is normally used as an antimetabolite and as an inhibitor of histamine and also is used in many syntheses.

The purpose of this paper is to report the examination of solid−liquid equilibria (SLE) in binary mixtures of imidazoles (1*H*-imidazole (I), 2-methyl-1*H*-imidazole (2MI), benzimidazole (BI), 2-methylbenzimidazole (2MBI), 2-phenylimidazole (2PhI), 4,5-diphenylimidazole (4,5-DPhI), or 2,4,5-triphenylimidazole (2,4,5-TPhI)) with organic solvents (dichloromethane, 1-chlorobutane, toluene, or 2-nitrotoluene) by using the synthetic method and liquid chromatography.

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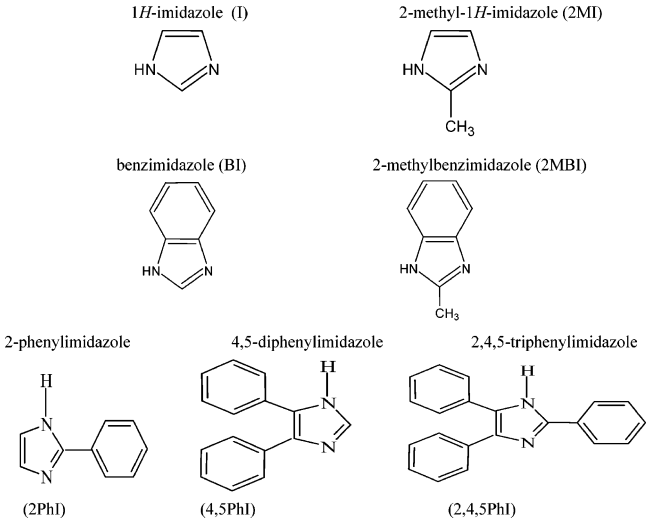
Table 1. Physical Constants of Pure Compounds: $T_{fus,1}$, Melting Temperature (This Work); $\Delta_{fus}H_1$, Molar Enthalpy of Fusion; $\Delta_{fus}C_{p,1}$, Heat Capacity Change at the Melting Temperature; and $V_m^{298.15}$, Molar Volume

component	$T_{fus,1}$/K	$T_{tr,1}$/K	$\Delta_{fus}H_1$/J·mol^{-1}	$\Delta_{tr}H_1$/J·mol^{-1}	$\Delta_{fus}C_{p,1}$/J·K^{-1}·mol^{-1}	$V_m^{298.15K}$/cm^3·mol^{-1}
1*H*-imidazole[a]	362.25		12 820[b]		24.17	61.6
2-methyl-1*H*-imidazole[a]	419.00	369.12	12 672	1590	41.05	76.1
benzimidazole[a]	445.51	384.43	20 472	710	49.09	89.2
2-methylbenzimidazole[a]	451.43	383.93	20 486	586	50.58	103.7
2-phenylimidazole[c]	422.85		17 900			114.0
4,5-diphenylimidazole	504.84		34 185			166.4
2,4,5-triphenylimidazole[c]	550.78	505.71	35 149	733		218.8

[a] From ref 2. [b] Other literature values: $\Delta_{fus}H_1$ = 11 184 J·mol^{-1} from ref 1; $\Delta_{fus}H_1$ = 12 821 J·mol^{-1} from ref 24; $\Delta_{fus}H_1$ = 12 500 J·mol^{-1} from ref 25. [c] From ref 3.

The molecular structures of the imidazoles, benzimidazoles, and phenylimidazoles under study are as follows:



The simple imidazole molecules with two hydrophilic nitrogen groups (1 and 3) could imply specific interactions between them and with solvent. The other five substances have a large aromatic group substituted on the imidazole ring, causing new interaction effects, manifested in an enhancement of the A−B interaction and in changing the solution structure. The molecular rearrangement in the solution depends on the possibility of hydrogen bond formation between the imidazole molecules themselves and between the imidazole and the chlorohydrocarbons or nitrotoluene or toluene, for which rather the $n-\pi$ interaction may be expected. The hydrogen bonds are responsible for the new crystal structure, described as blocks of imidazole salt with mono-, di-, or tetracarboxylic acids.[23] The solubilities of BI and 2PhI in water, where the specific interaction was expected, were presented earlier.[3]

Experimental Section

Herein are reported the origins of the chemicals, the Chemical Abstracts Service registry numbers (provided by the authors), and the corresponding mass percent purities: 1*H*-imidazole (288-32-4, Koch-Light Laboratory, 99%), 2-methyl-1*H*-imidazole (693-98-1, Koch-Light Laboratory, 99%), benzimidazole (51-17-2, Koch-Light Laboratory, 98%), 2-methylbenzimidazole (615-15-6, Koch-Light Laboratory, 98%), 2-phenylimidazole (670-96-2, Koch-Light Laboratory, 98%), 4,5-diphenylimidazole, 2,4,5-triphenylimidazole (484-47-9, Koch-Light Laboratory, 98%), dichloromethane (99.6%, Aldrich), 1-chlorobutane (99.5%, Aldrich), toluene (99%, OBR PR, Płock), 2-nitrotoluene (99.5%+, Aldrich). Solutes were dried for 24 h in a vacuum before use at 330 K. All solvents were fractionally distilled over different drying reagents to a mass fraction purity better than 99.8%.

Table 2. Molar Volume, V_m (298.15 K), for Solvents

solvent	$V_m^{298.15K}$ [a]/cm^3·mol^{-1}
1-chlorobutane	104.7
dichloromethane	64.0
toluene	106.8
2-nitrotoluene	118.0

[a] From ref 26.

Liquids were stored over freshly activated molecular sieves of type 4A (Union Carbide). All compounds were checked by GLC analysis, and no significant impurities were found. Analysis, using the Karl Fischer technique, showed that the water contamination in the solvents was less than 0.03 mass %. The molar enthalpy of fusion of 4,5-diphenylimidazole was measured using a Pyris 1 differential scanning calorimeter from Perkin-Elmer. Fusion experiments were carried out at the scan rate 2 K·min^{-1}. The instrument was calibrated against a 99.9999 mol % purity indium sample. Physical properties of pure imidazoles and solvents are collected in Tables 1 and 2.

Synthetic Method. Solid−liquid equilibrium temperatures were determined using a method described in detail previously.[27] 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. Mixtures were prepared by weighing the pure components to within 2×10^{-4} g. The crystal disappearance temperatures, detected visually, were measured with an electronic thermometer P 500 (DOSTMANN electronic GmbH) with the probe totally immersed in the thermostating liquid. The thermometer was calibrated on the basis of the ITS-90 temperature scale. The uncertainty of temperature measurements was ±0.05 K, and that of the mole fraction did not exceed ±0.0005.

High-Performance Liquid Chromatography (HPLC). For the very low solubilities another method of saturated solution analysis at constant temperature has to be used. HPLC is a popular method of analysis because it is easy to learn and use and is not limited by the volatility or stability of the sample compound. HPLC instrumentation includes a pump, injector, column, detector, and data system. The heart of the system is the column where separation occurs. Since the stationary phase is composed of micrometer size porous particles, a high-pressure pump is required to move the mobile phase through the column. The chromatographic process begins by injecting the solute onto the top of the column. Separation of components occurs as the analytes and mobile phase are pumped through the column. Eventually, each component elutes from the column as a narrow band (or peak) on the recorder. Detection of the eluting components is important, and this can be either selective or universal, depending upon the detector used. The response of the detector to each component is displayed on a chart recorder or computer screen and is known as a chromatogram. To collect, store, and

Table 3. Experimental Solid−Liquid Equilibrium Temperatures, *T*, for {2-Methyl-1*H*-imidazole (1) + Solvent (2)} (Synthetic Method)[a]

x_1	T/K	γ_1	x_1	T/K	γ_1	x_1	T/K	γ_1
				1-Chlorobutane				
0.0010	300.36	217.6	0.0083	335.72	46.3	0.0262	345.97	17.1
0.0012	304.07	188.6	0.0091	336.55	43.0	0.0283	346.47	16.0
0.0016	308.40	151.2	0.0095	336.95	41.4	0.0309	346.87	14.7
0.0019	310.55	133.3	0.0101	337.55	39.2	0.0340	348.06	13.6
0.0023	315.79	122.9	0.0103	337.85	38.6	0.0349	348.16	13.3
0.0033	320.61	92.6	0.0110	338.24	36.4	0.0361	348.26	12.8
0.0036	322.81	86.3	0.0123	338.95	32.8	0.0378	348.76	12.3
0.0040	325.58	81.7	0.0139	340.05	29.5	0.0399	348.96	11.7
0.0046	327.09	73.5	0.0145	340.35	28.4	0.0405	349.06	11.5
0.0052	329.55	67.4	0.0150	340.65	27.6	0.0495	349.59	9.5
0.0058	330.24	61.1	0.0158	340.98	26.3	0.0515	350.15	9.2
0.0064	331.87	56.9	0.0170	341.58	24.7	1.0000	419.00	1.0
0.0075	334.67	50.4	0.0197	342.68	21.7			
				Dichloromethane				
0.0231	296.48	9.6	0.1140	324.47	3.0	0.2380	351.88	2.1
0.0270	299.45	8.7	0.1160	325.58	3.0	0.2404	352.65	2.1
0.0361	302.86	6.9	0.1277	328.52	2.8	0.2455	353.38	2.1
0.0372	303.82	6.8	0.1347	329.60	2.7	0.2537	354.67	2.0
0.0398	304.47	6.4	0.1486	332.41	2.6	0.2577	355.45	2.0
0.0448	307.08	5.9	0.1538	333.23	2.5	0.2683	357.19	2.0
0.0547	308.93	5.0	0.1600	335.45	2.5	0.2734	358.09	2.0
0.0565	309.67	4.9	0.1665	336.75	2.5	0.2840	359.57	1.9
0.0673	312.47	4.3	0.1727	338.07	2.4	0.2981	361.78	1.9
0.0733	313.88	4.0	0.1877	340.65	2.3	0.3043	363.06	1.9
0.0813	316.97	3.8	0.1974	342.73	2.2	0.3166	365.49	1.8
0.0898	318.86	3.5	0.2017	344.47	2.2	0.3225	366.87	1.8
0.0899	319.28	3.6	0.2146	347.95	2.2	0.3318	368.27	1.8
0.1031	321.45	3.2	0.2203	348.75	2.2	0.3425	370.31	1.8
0.1094	323.12	3.1	0.2293	350.07	2.1	1.0000	419.00	1.0
				Toluene				
0.0042	324.47	76.1	0.0182	344.38	24.1			
0.0053	334.22	71.2	0.0217	345.24	20.4	0.1120	354.34	4.5
0.0056	333.27	66.0	0.0266	346.10	16.9	0.1142	354.34	4.4
0.0060	335.83	64.0	0.0283	346.50	16.0	0.1230	354.72	4.1
0.0062	338.09	64.1	0.0355	347.69	12.9	0.1382	355.15	3.7
0.0070	338.78	58.0	0.0355	347.56	12.9	0.1584	355.88	3.2
0.0088	340.09	46.7	0.0451	348.65	10.3	0.2014	356.88	2.6
0.0095	340.85	44.0	0.0477	349.01	9.8	0.2105	357.15	2.5
0.0109	342.28	38.8	0.0562	350.07	8.4	0.2118	357.15	2.5
0.0110	342.05	38.5	0.0645	350.85	7.4	0.2351	357.65	2.2
0.0128	342.85	33.4	0.0681	351.19	7.1	0.2644	358.50	2.0
0.0149	343.26	29.0	0.0837	352.58	5.9	1.0000	419.00	1.0
0.0170	343.92	25.5	0.0904	353.15	5.5			
0.0172	344.05	25.3	0.0955	353.49	5.2			
				2-Nitrotoluene				
0.0668	333.97	5.6	0.3472	367.67	1.7	0.6965	397.06	1.2
0.0858	341.06	4.9	0.3563	368.26	1.7	0.7244	400.37	1.2
0.1335	347.74	3.4	0.3873	370.45	1.6	0.7666	402.82	1.1
0.1805	353.97	2.8	0.3923	371.57	1.6	0.7968	405.19	1.1
0.1998	355.88	2.6	0.4176	373.46	1.5	0.8200	406.36	1.1
0.2315	358.34	2.3	0.4419	375.65	1.5	0.8809	408.88	1.0
0.2546	359.97	2.1	0.4475	375.87	1.5	0.9131	410.75	1.0
0.2723	361.08	2.0	0.5288	384.15	1.3	0.9430	413.23	1.0
0.3142	365.17	1.8	0.5373	386.17	1.4	0.9624	415.16	1.0
0.3238	366.53	1.8	0.5930	282.40	1.3	1.0000	419.00	1.0
0.3374	368.42	1.8	0.5970	390.13	1.3			
0.3429	367.13	1.7	0.6157	392.67	1.3			

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

Table 4. Experimental Solid−Liquid Equilibrium Temperatures, *T*, for {Benzimidazole (1) + Solvent (2)} (Synthetic Method)[a]

x_1	T/K	γ_1	x_1	T/K	γ_1	x_1	T/K	γ_1
				1-Chlorobutane				
0.0009	296.33	65.1	0.0015	326.56	87.9	0.0020	340.19	86.5
0.0009	296.72	65.1	0.0015	327.45	88.0	0.0021	340.99	85.9
0.0009	300.7	71.3	0.0015	328.37	87.6	0.0021	341.51	86.4
0.0010	305.34	76.2	0.0016	329.88	89.0	0.0021	341.90	85.9
0.0010	308.99	80.0	0.0016	330.43	89.0	0.0022	342.03	84.2
0.0010	308.24	78.4	0.0016	331.91	89.3	0.0022	342.28	83.5
0.0011	311.77	82.1	0.0017	332.89	89.2	0.0022	342.57	82.9
0.0011	312.54	80.8	0.0017	333.77	88.9	0.0023	342.58	82.2
0.0011	313.83	82.8	0.0017	334.83	89.5	0.0023	342.97	81.4
0.0012	316.32	84.5	0.0018	335.59	90.0	0.0023	343.46	81.9
0.0012	317.57	85.1	0.0018	336.58	89.0	0.0023	343.27	80.9
0.0013	318.76	82.9	0.0018	336.95	88.8	0.0023	343.63	80.8
0.0013	320.09	85.0	0.0019	337.61	87.7	0.0024	343.80	79.8
0.0013	321.98	85.7	0.0019	338.57	88.2	0.0024	344.33	78.7
0.0014	322.65	84.6	0.0020	339.09	87.4	1.0000	445.51	1.0
0.0014	324.64	86.9	0.0020	339.57	87.0			
				Dichloromethane				
0.0034	306.08	22.3	0.0184	347.56	11.2	0.0287	353.47	8.1
0.0041	308.62	20.1	0.0191	348.06	10.9	0.0294	352.95	7.8
0.0048	314.57	20.0	0.0195	347.97	10.6	0.0310	353.00	7.4
0.0054	318.88	19.5	0.0206	348.46	10.1	0.0319	352.96	7.2
0.0064	324.42	19.0	0.0213	348.97	9.9	0.0329	353.94	7.1
0.0078	328.25	17.2	0.0223	349.45	9.6	0.0341	353.67	6.8
0.0105	335.54	15.1	0.0236	350.40	9.2	0.0354	354.86	6.8
0.0112	336.29	14.3	0.0244	350.89	9.0	0.0380	355.55	6.4
0.0139	340.65	12.8	0.0253	351.35	8.8	0.0403	356.53	6.1
0.0149	343.45	12.6	0.0263	352.08	8.6	0.0412	357.38	6.1
0.0163	345.18	12.0	0.0268	352.24	8.4	1.0000	445.51	1.0
0.0178	346.55	11.3	0.0275	352.26	8.2			
				Toluene				
0.0009	297.97	70.6	0.0039	348.55	54.1	0.0058	360.36	46.2
0.0012	314.02	78.4	0.0041	350.35	52.8	0.0062	362.20	44.9
0.0014	318.98	75.1	0.0043	351.18	51.6	0.0064	363.15	44.0
0.0017	324.75	73.2	0.0044	352.67	52.1	0.0065	363.65	43.9
0.0019	327.45	68.7	0.0046	353.85	51.3	0.0066	363.85	43.3
0.0022	329.85	64.0	0.0048	355.12	50.4	0.0067	363.85	42.6
0.0026	337.55	63.7	0.0050	355.97	49.1	0.0075	365.23	39.3
0.0032	342.25	57.2	0.0052	357.18	47.8	1.0000	445.51	1.0
0.0035	345.85	57.0	0.0055	358.95	47.0			
				2-Nitrotoluene				
0.0105	316.65	9.6	0.0894	362.76	3.1	0.3523	397.95	1.5
0.0144	323.17	8.2	0.0969	364.95	3.0	0.4249	407.05	1.4
0.0209	330.58	6.7	0.1087	367.45	2.8	0.4557	410.65	1.4
0.0264	335.86	6.0	0.1323	372.40	2.5	0.4911	414.15	1.3
0.0311	339.45	5.5	0.1488	374.25	2.3	0.5111	416.25	1.3
0.0414	345.19	4.7	0.1937	381.70	2.0	0.5598	421.85	1.3
0.0479	347.76	4.3	0.2267	384.01	1.8	0.6379	428.55	1.2
0.0505	349.78	4.3	0.2494	384.55	1.7	0.6777	430.95	1.2
0.0557	351.74	4.0	0.2553	383.55	1.6	0.7725	438.05	1.2
0.0629	354.05	3.7	0.2691	384.95	1.5	0.7987	438.35	1.1
0.0720	357.85	3.5	0.2819	386.35	1.5	1.0000	445.51	1.0
0.0753	359.15	3.4	0.3041	390.67	1.5			

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

analyze the chromatographic data, a computer is frequently used.

Quantification of compounds by HPLC is the process of determining the unknown concentration of a compound in a known solution. It involves injecting a series of known concentrations of the standard compound solution onto the HPLC for detection. The chromatograph of these known concentrations will give a series of peaks that correlate with the concentration of the compound injected.

Using the area of a triangle equation to calculate the area under each peak, a set of data is generated to develop a calibration curve. Graphing peak area versus the concentration of the sample solution does this. Most graphs can be generated using a computer software program. From this graphing software, a best-fit line can be derived, and the equation of that line can be determined. This equation of a line, $y = mx + b$, generated by the data, is the calibration curve equation. The equation of the line is then used in the following manner: a sample of unknown concentration x (x-axis of calibration curve) is injected onto the HPLC; the chromatograph gives a peak output of area y (y-axis of the calibration curve). The area, y, is then in the equation of a line $y = mx + b$ from the calibration curve, and the concentration is found by solving the equation for x. The uncertainties of temperature measurements and of the mole fraction were ±0.05 K and $\pm 2 \times 10^{-8}$, respectively.

Results and Discussion

Tables 3−5 list the direct experimental results of the SLE, temperatures, T versus x_1, the mole fraction of the imidazoles, and γ_1, the experimental activity coefficients in the saturated solution for the investigated systems, obtained by the synthetic method. The values of the activity coefficients were taken from the correlation equations, which could be used for a large number of the experimental points.

Table 5. Experimental Solid−Liquid Equilibrium Temperatures, *T*, for {2-Methylbenzimidazole (1) + Solvent (2)} (Synthetic Method)[a]

x_1	T/K	γ_1	x_1	T/K	γ_1	x_1	T/K	γ_1
1-Chlorobutane								
0.0005	290.39	86.2	0.0008	315.07	111.7	0.0016	331.57	83.4
0.0005	291.68	87.9	0.0008	316.34	111.3	0.0018	332.83	79.0
0.0006	293.51	91.1	0.0009	317.71	109.9	0.0019	334.91	75.9
0.0006	298.82	100.7	0.0009	319.44	108.6	0.0021	336.48	72.9
0.0006	302.58	106.4	0.0009	320.03	109.0	0.0023	338.33	69.6
0.0007	305.53	108.3	0.0010	322.65	109.3	0.0025	340.17	66.3
0.0007	307.87	105.6	0.0010	323.75	109.0	0.0028	342.91	61.4
0.0007	308.55	107.5	0.0011	324.20	105.1	0.0031	344.47	58.6
0.0007	309.66	109.2	0.0012	325.97	100.4	0.0032	345.15	57.7
0.0007	311.39	111.2	0.0013	328.16	93.1	1.0000	451.43	1.0
0.0008	312.96	111.3	0.0014	328.95	90.1			
Dichloromethane								
0.0065	307.95	11.6	0.0538	342.72	3.2	0.0983	355.37	2.3
0.0075	313.33	11.5	0.0591	344.78	3.1	0.1051	357.13	2.2
0.009	315.75	10.3	0.0644	346.27	2.9	0.1075	358.12	2.2
0.0108	317.93	9.0	0.0684	348.04	2.8	0.1113	359.56	2.2
0.0142	322.39	7.6	0.0749	349.56	2.7	0.1165	360.18	2.1
0.0196	326.96	6.2	0.0786	350.28	2.6	0.1188	360.90	2.1
0.0246	331.88	5.5	0.0818	350.67	2.5	0.1222	361.16	2.1
0.0296	333.19	4.7	0.0874	352.23	2.4	0.1254	362.16	2.0
0.0352	336.75	4.3	0.0903	353.76	2.4	1.0000	451.43	1.0
0.0432	339.43	3.7	0.0928	353.95	2.3			
0.0463	339.67	3.5	0.0956	354.67	2.3			
Toluene								
0.0008	307.98	98.9	0.0029	336.62	52.8	0.0075	358.18	31.6
0.0008	311.40	100.4	0.0029	336.66	52.1	0.0084	361.28	30.3
0.0011	314.51	85.0	0.0032	338.78	50.1	0.0094	363.55	28.3
0.0011	317.11	83.6	0.0033	339.65	49.5	0.0095	363.61	28.0
0.0013	319.21	77.9	0.0034	340.35	48.4	0.0097	364.35	27.6
0.0014	319.91	72.5	0.0035	340.95	47.7	0.0099	364.48	27.2
0.0016	323.56	68.6	0.0036	341.85	46.9	0.0105	366.09	26.4
0.0019	326.75	62.8	0.0037	342.15	46.7	0.0111	367.16	25.6
0.0021	328.66	59.8	0.0040	344.28	44.7	0.0113	367.78	25.4
0.0022	329.35	59.4	0.0046	346.88	40.8	0.0118	368.77	24.8
0.0024	332.55	57.8	0.0051	348.93	38.9	0.0122	369.69	24.3
0.0026	334.10	54.8	0.0054	351.15	38.3	0.0130	371.03	23.5
0.0027	334.97	54.2	0.0057	351.38	36.5	1.0000	451.43	11.0
0.0028	335.65	53.5	0.0064	354.36	34.4			
2-Nitrotoluene								
0.0092	310.87	8.8	0.0945	357.27	2.5	0.2792	394.46	1.6
0.0137	317.35	7.0	0.0980	358.16	2.4	0.2946	397.37	1.6
0.0194	323.56	5.8	0.1043	361.05	2.4	0.3052	398.36	1.6
0.0238	329.18	5.3	0.1091	363.65	2.4	0.3141	399.19	1.5
0.0283	335.93	5.3	0.1145	364.75	2.4	0.3212	400.45	1.5
0.0351	338.96	4.5	0.1191	367.35	2.4	0.3448	402.64	1.5
0.0370	339.85	4.4	0.1236	369.25	2.4	0.3616	404.66	1.5
0.0401	341.23	4.2	0.1263	369.25	2.3	0.3807	406.56	1.5
0.0447	343.18	3.9	0.1317	370.85	2.3	0.3915	407.88	1.4
0.0483	344.62	3.7	0.135	371.32	2.3	0.3998	408.97	1.4
0.0520	345.77	3.5	0.1365	372.15	2.3	0.4184	409.93	1.4
0.0587	347.17	3.2	0.1452	374.33	2.2	0.4410	412.06	1.3
0.0625	348.56	3.1	0.1596	376.46	2.1	0.4576	414.18	1.3
0.0670	349.44	3.0	0.1714	378.36	2.0	0.4827	416.69	1.3
0.0714	350.37	2.8	0.1873	379.05	1.9	0.4920	417.55	1.3
0.0741	351.53	2.8	0.2128	383.42	1.8	0.5691	421.70	1.2
0.0773	352.36	2.7	0.2168	385.36	1.8	0.6352	427.62	1.2
0.0800	353.18	2.7	0.2335	387.86	1.7	1.0000	451.43	1.0
0.0844	354.83	2.6	0.2511	390.00	1.7			
0.0881	356.07	2.6	0.2557	390.17	1.6			

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

Table 6. Experimental Solid−Liquid Equilibrium Temperatures, *T*, for {1*H*-Imidazole (1) + Solvent (2)} (HPLC Method)

10^5x_1	T/K	10^5x_1	T/K
1-Chlorobutane		Toluene	
0.804	298.15	3.70	298.15
0.933	303.15	4.85	303.15
0.112	313.15	6.76	313.15
Dichloromethane		2-Nitrotoluene	
2.76	298.15	1.24	298.15
3.19	303.15	1.29	303.15
6.57	308.15	1.42	313.15
7.02	313.15		

The solubility of a solid 1 in a liquid showing the solid−solid phase transition before fusion may be expressed in a very general manner by eq 1.[28,29] The solubility equation

Table 7. Experimental Solid−Liquid Equilibrium Temperatures, *T*, for {2-Phenylimidazole (1) + Solvent (2)} (HPLC Method)

10^6x_1	T/K	10^6x_1	T/K
1-Chlorobutane		Toluene	
2.14	298.15	5.97	298.15
3.65	303.15	6.32	303.15
4.21	313.15	6.86	313.15
Dichloromethane		2-Nitrotoluene	
14.6	298.15	2.70	298.15
14.7	303.15	2.91	303.15
15.5	313.15	3.89	313.15

Table 8. Experimental Solid−Liquid Equilibrium Temperatures, *T*, for {4,5-Diphenylimidazole (1) + Solvent (2)} (HPLC Method)

10^6x_1	T/K	10^6x_1	T/K
1-Chlorobutane		Toluene	
1.26	298.15	3.01	298.15
1.38	303.15	3.33	303.15
1.76	313.15	3.57	313.15
Dichloromethane		2-Nitrotoluene	
1.85	298.15	1.91	298.15
2.98	303.15	1.91	303.15
4.20	313.15	1.95	313.15

Table 9. Experimental Solid−Liquid Equilibrium Temperatures, *T*, for {2,4,5-Triphenylimidazole (1) + Solvent (2)} (HPLC Method)

10^6x_1	T/K	10^6x_1	T/K
1-Chlorobutane		Toluene	
1.54	298.15	1.95	298.15
1.97	303.15	2.04	303.15
2.18	313.15	2.36	313.15
Dichloromethane			
1.41	298.15		
1.73	303.15		
2.11	313.15		

for temperatures below that of the phase transition must include the effect of the transition. The result for the first-order transition is

$$-\ln x_1\gamma_1 = \frac{\Delta_{fus}H_1}{R}\left(\frac{1}{T}-\frac{1}{T_{fus,1}}\right)+\frac{\Delta_{tr}H_1}{R}\left(\frac{1}{T}-\frac{1}{T_{tr,1}}\right)-\frac{\Delta_{fus}C_{p,1}}{R}\left(\ln\frac{T}{T_{fus,1}}+\frac{T_{fus,1}}{T}-1\right) \quad (1)$$

where x_1, γ_1, $\Delta_{fus}H_1$, $\Delta_{fus}C_{p,1}$, $T_{fus,1}$, and T stand for mole fraction, activity coefficient, enthalpy of fusion, difference in solute heat capacity between the solid and the liquid at the melting temperature, melting temperature of the solute (1), and equilibrium temperature, respectively.

$\Delta_{tr}H_1$ and $T_{tr,1}$ stand for the enthalpy of the solid−solid transition and the transition temperature of the solute, respectively. Equation 1 is valid for simple eutectic mixtures with complete immiscibility in the solid phase.

In this study three methods were used to fit the solute activity coefficients, γ_1, to the so-called correlation equations that describe the Gibbs excess energy, G^E: the Wilson,[30] UNIQUAC,[31] and NRTL[32] models. The exact mathematical forms of the equations have been presented in our previous paper.[33]

The parameters of the equations were fitted by an optimization technique. The objective function was as follows

$$F(A_1A_2) = \sum_{i=1}^{n} w_i^{-2}[\ln x_{1i}\gamma_{1i}(T_i,x_{1i},A_1A_2) - \ln a_{1i}]^2 \quad (2)$$

where $\ln a_{1i}$ denotes an "experimental" value of the

Table 10. Correlation of the Solubility Data (SLE) of {Imidazoles (1) + Solvent (2)} Mixtures by Means of the Wilson, UNIQUAC, and NRTL Equations: Values of Parameters and Measures of Deviations

	parameters/J·mol^{-1}						deviations (σ_T/K)		
	Wilson		UNIQUAC		NRTL				
solvent	$g_{12}-g_{11}$	$g_{12}-g_{22}$	Δu_{12}	Δu_{21}	Δg_{12}	Δg_{21}	Wilson	UNIQUAC	NRTL
				2-Methyl-1*H*-imidazole					
1-chlorobutane	14532.44	−223.26	−2300.67	10132.53	−521.31	13015	1.09	7.41	6.26[a]
dichloromethane	4246.38	1321.74	96.98	2502.73	5619.22	5526.05	5.69	6.13	3.22[b]
toluene	15079.53	−226.82			5068.63	10276.73	1.40		6.72[c]
2-nitrotoluene	6043.64	440.59	−634.46	3523.66	4156.87	6247.94	3.53	4.20	1.30[d]
				Benzimidazole					
1-chlorobutane	10127.55	165270.88	93646.29	2533.47	10933.05	10518.16	6.26	4.97	5.86[a]
dichloromethane	8461.64	372.84	−1859.82	6552.15	−247.31	8876.42	1.68	1.06	1.29[c]
toluene	9593.99	97301.96	2953.15	3171.17	10108.90	9541.95	2.15	1.93	1.82[e]
2-nitrotoluene	6970.75	−1007.18	−1591.05	4592.25	4389.28	5705.87	5.00	5.76	2.55[f]
				1-Methylbenzimidazole					
1-chlorobutane	9623.17	13931.88	2303.42	3046.75	6876.01	10126.10	4.42	4.49	4.42[g]
dichloromethane	7722.26	−181.32	−1748.20	5106.43	492.05	6401.37	1.95	3.25	2.35[h]
toluene	11436.27	565.44	−2890.20	9698.37	−1983.38	13161.65	0.85	3.34	5.06[i]
2-nitrotoluene	5262.14	−449.24	−1189.04	3183.09	1868.67	4154.84	4.36	5.00	3.67[f]

[a] Calculated with the parameter $\alpha = 0.45$. [b] Calculated with $\alpha = 0.78$. [c] Calculated with $\alpha = 0.60$. [d] Calculated with $\alpha = 0.70$. [e] Calculated with $\alpha = 0.43$. [f] Calculated with $\alpha = 0.95$. [g] Calculated with $\alpha = 0.47$. [h] Calculated with $\alpha = 0.90$. [i] Calculated with $\alpha = 0.15$.

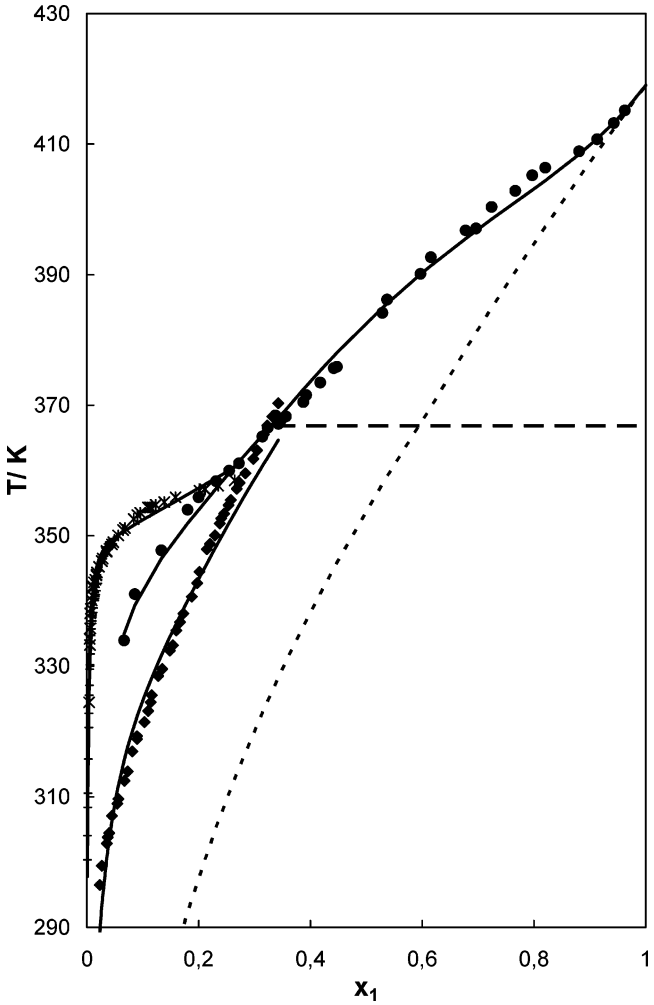


Figure 1. Solubility of 2-methyl-1*H*-imidazole in (+) chlorobutane, (◆) dichloromethane, (∗) toluene, or (●) 2-nitrotoluene; points are the experimental values; solid lines are from the correlation by the Wilson equation; the dashed line designates the solid−solid phase transition; the dotted line is the ideal solubility.

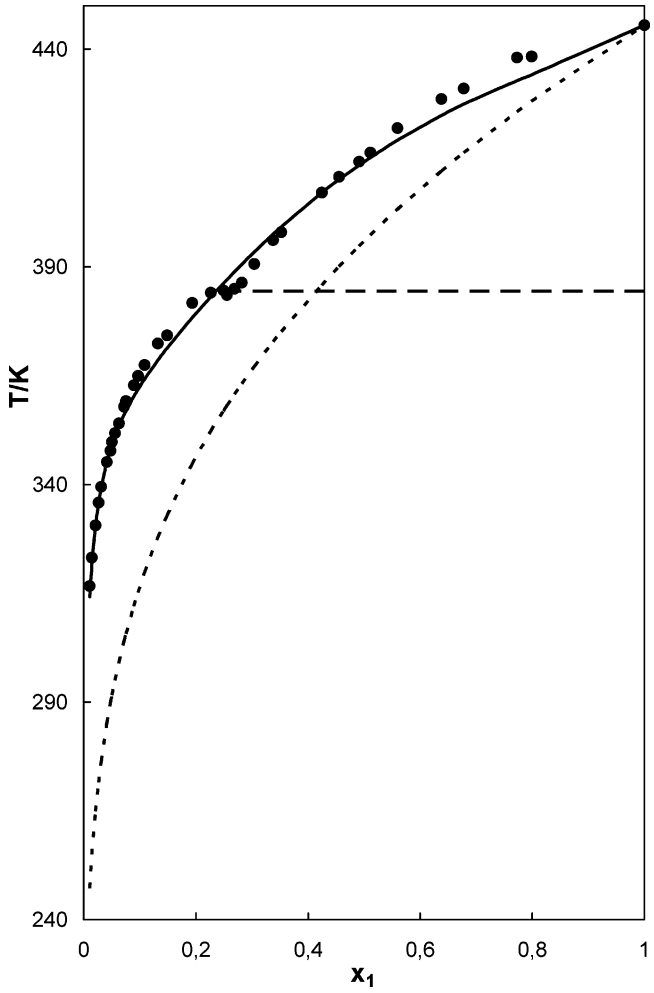


Figure 2. Solubility of benzimidazole in 2-nitrotoluene: points are the experimental values; the solid line is from the correlation by the NRTL equation; the dashed line designates the solid−solid phase transition; the dotted line is the ideal solubility.

logarithm of the solute activity, taken as the left-hand side of eq 1, w_i is the weight of an experimental point, A_1 and A_2 are the two adjustable parameters of the correlation equations, i denotes the ith experimental point, and n is the number of experimental data. The weights were calculated by means of the error propagation formula

$$w_i^2 = (\partial \ln x_1\gamma_1 - \partial \ln a_i/\partial T)_{T=T_i}^2(\Delta T_i)^2 + (\partial \ln x_1\gamma_1/\partial x_1)_{x_1=x_{1i}}^2(\Delta x_{1i})^2 \quad (3)$$

where ΔT and Δx_1 are the estimated errors in T and x_{1i}, respectively.

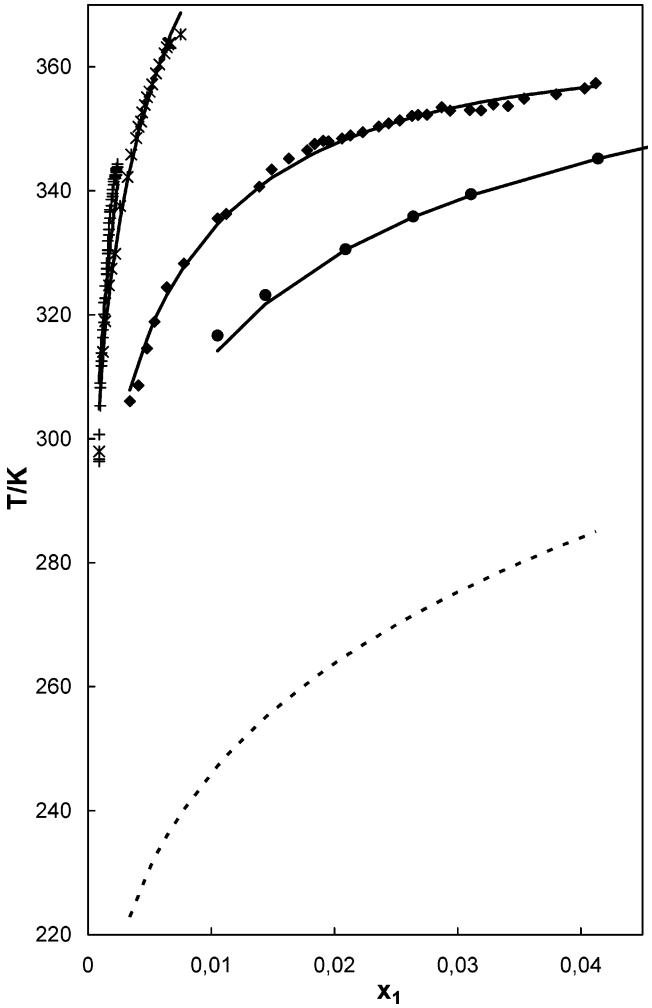


Figure 3. Solubility of benzimidazole in (+) chlorobutane, (◆) dichloromethane, (∗) toluene, or (●) 2-nitrotoluene; points are the experimental values; solid lines are from the correlation by the Wilson equation; the dotted line designates the ideal solubility.

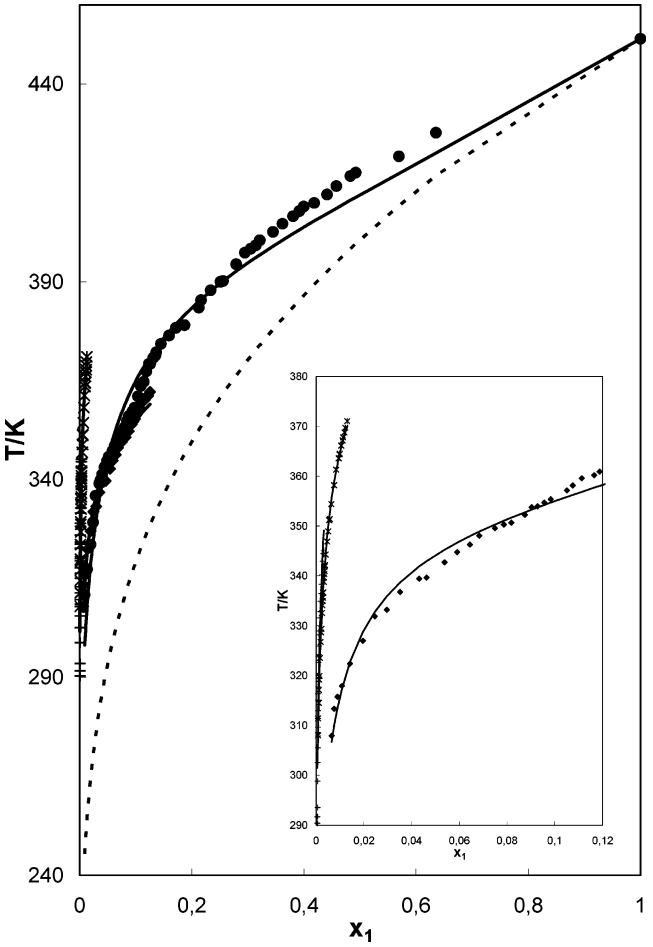


Figure 4. Solubility of 2-methylbenzimidazole in (+) chlorobutane, (◆) dichloromethane, (∗) toluene, or (●) 2-nitrotoluene; points are the experimental values; solid lines are from the correlation by the Wilson equation; the dotted line designates the ideal solubility.

According to the above formulation, the objective function was obtained by solving the nonlinear equation (eq 1), using the Marquardt method of minimization.[34] The root-mean-square deviation of temperature (σ_T defined by eq 4) was used as a measure of the goodness of the solubility correlation.

$$\sigma_T = \left(\sum_{i=1}^{n} \frac{((T_i)^{\mathrm{exp}} - (T_i)^{\mathrm{cal}})^2}{n-2} \right)^{1/2} \tag{4}$$

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 equation were obtained by means of the following simple relationships[35]

$$r_i = 0.029281 V_{\mathrm{m}} \tag{5}$$

$$q_i = \frac{(z-2) r_i}{z} + \frac{2(1-l_i)}{z} \tag{6}$$

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 $l_i = 1$ for cyclic molecules. The calculations were carried out by the use of the data set presented in Tables 1 and 2. Unfortunately, it was not possible to provide the calculations for the experimental points obtained by the HPLC method. First of all, the number of experimental points was not sufficient for the correlation, and second, the root-mean-square deviations for such small solubilities are usually very high. The experimental results for 1*H*-imidazole, 2-phenylimidazole, 4,5-diphenylimidazole, and 2,4,5-triphenylimidazole are presented in Tables 6−9.

Table 10 lists the results of fitting the solubility curves by the three equations used: Wilson, UNIQUAC, and NRTL. For the 12 systems presented in this work the best description of solid−liquid equilibrium was given by the two-parameter Wilson equation with the average standard deviation $\sigma_T = 3.2$ K. These results are worse than those in the binary mixtures of imidazoles[1] or benzimidazoles[7] with alcohols or ketones.[5,6]

The experimental SLE phase diagrams investigated in this work are characterized mainly by the following:

(i) High positive deviations from ideality were found for every mixture; thus, the solubility is much lower than the ideal one, $\gamma_1 \gg 1$ (see the values of the activity coefficients in Tables 3−5 and Figures 1−4 for imidazoles).

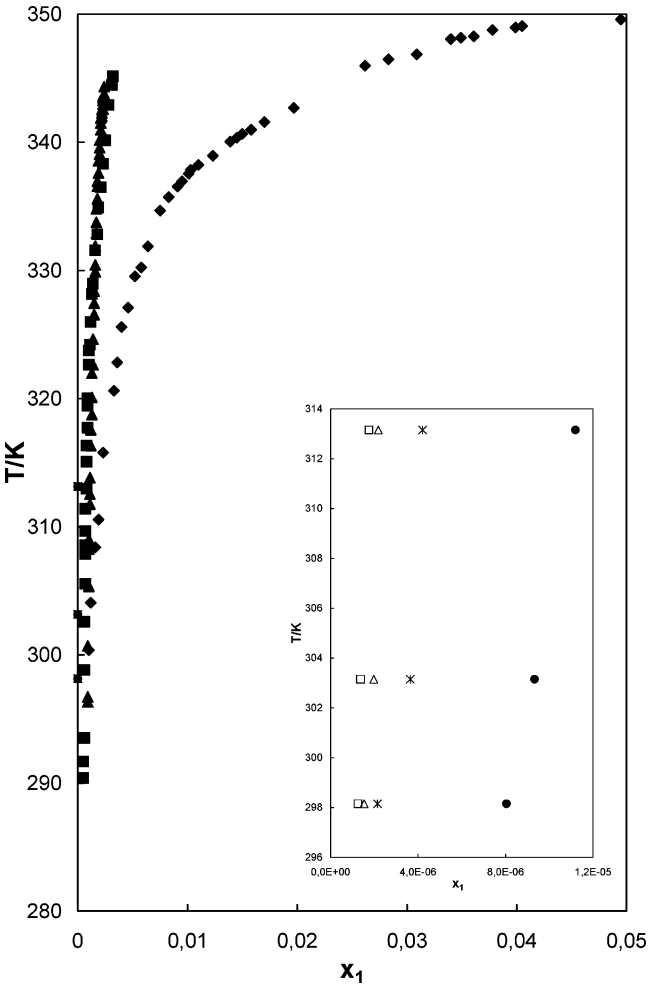


Figure 5. Solubility of (●) 1*H*-imidazole, (◆) 2-methyl-1*H*-imidazole, (▲) benzimidazole, (■) 2-methylbenzimidazole, (∗) 2-phenylimidazole, (○) 4,5-diphenylimidazole, or (△) 2,4,5-triphenylimidazole in 1-chlorobutane; points are the experimental values.

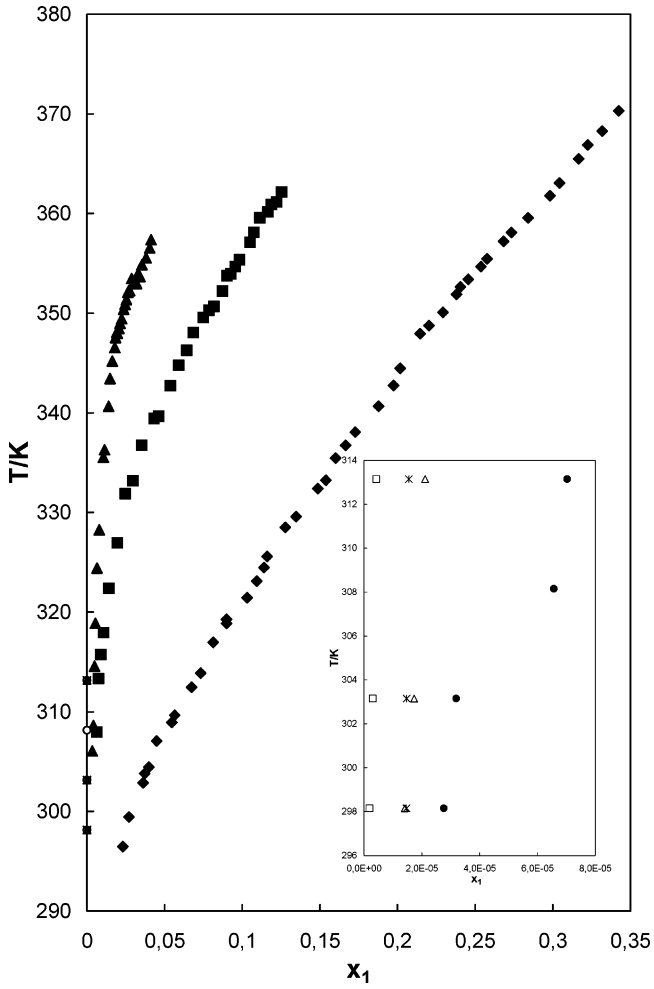


Figure 6. Solubility of (●) 1*H*-imidazole, (◆) 2-methyl-1*H*-imidazole, (▲) benzimidazole, (■) 2-methylbenzimidazole, (∗) 2-phenylimidazole, (○) 4,5-diphenylimidazole, or (△) 2,4,5-triphenylimidazole in dichloromethane; points are the experimental values.

(ii) The liquidus curves of 2MI, BI, and 2MBI in dichloromethane and 2-nitrotoluene exhibit similar shapes; the differences in solubilities are small, and for all solvents the solubility increases in order chlorobutane < toluene < 2-nitrotoluene < dichloromethane (see Figures 1−4), with the exception of benzimidazole, for which the solubility in nitrotoluene is higher than that in dichloromethane (see Figure 3).

(iii) The solubilities of 2PhI, 4,5DPhI, and 2,4,5TPhI were compared with those of I, for which it was known from our previous work[1,2,4,5] that the solubility in different solvents (water, alcohols, ethers, or ketones) is much higher than those of benzimidazoles or phenylimidazoles. The discussion of the fusion temperatures and enthalpies presented in Table 1 confirms for us the conviction that the solubilities of these bulky molecules will be very small. In this work it can be observed that in low concentration solutions the solubility of phenylimidazoles is much lower than that of I. In every solvent used here (1-chlorobutane, dichloromethane, toluene, and 2-nitrotoluene) the solubility of 2-phenylimidazole is higher than that of 4,5DPhI. However, it was noted that the solubilities of 2,4,5TPhI in 1-chlorobutane, dichloromethane, and toluene were higher than those of 4,5DPhI (see Figures 5−8). In every system the solubilities of benzimidazoles were higher than those of phenylimidazoles.

Conclusions

The results presented in this paper indicate that the solubilities of imidazoles are controlled by the strengths of specific interactions. The competition between hydrogen bonded imidazole molecules and the A−B association with solvent molecules is an important factor determining the phase behavior of imidazoles. Thus, imidazoles, benzimidazoles, and phenylimidazoles were chosen for this experiment not only because of the large hydrophobic aromatic groups but also for the known specific interactions of nitrogen atoms, or the hydrogen atom, with solvent. The structure of the solution and the molecular rearrangements were observed mainly in 2-nitrotoluene and dichloromethane. Besides the $n-\pi$ interaction between the nitrogen atom of the imidazole ring and aromatic ring, the interaction between the hydrogen atom of imidazole and the oxygen atoms of the nitro group can be very strong. The solubilities of 2MI,[1] BI,[7] and 2MBI[7] in dichloromethane and nitrobenzene are much lower than those in alcohols and much higher than those in ethers[6] and are comparable to the solubility in ketones.[6] Thus, the interactions with

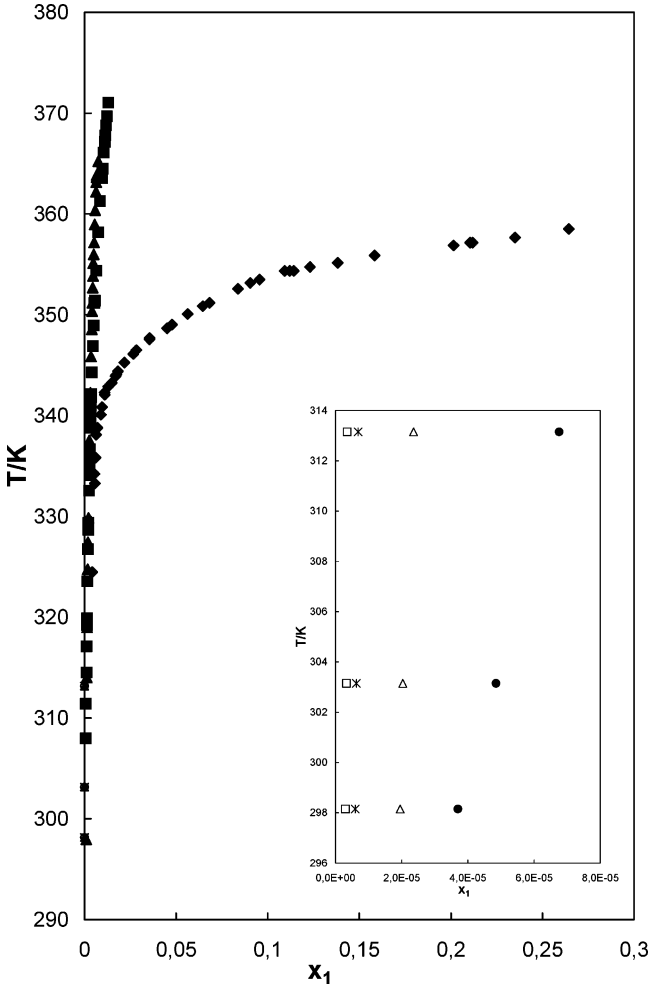


Figure 7. Solubility of (●) 1*H*-imidazole, (◆) 2-methyl-1*H*-imidazole, (▲) benzimidazole, (■) 2-methylbenzimidazole, (∗) 2-phenylimidazole, (○) 4,5-diphenylimidazole, or (△) 2,4,5-triphenylimidazole in toluene; points are the experimental values.

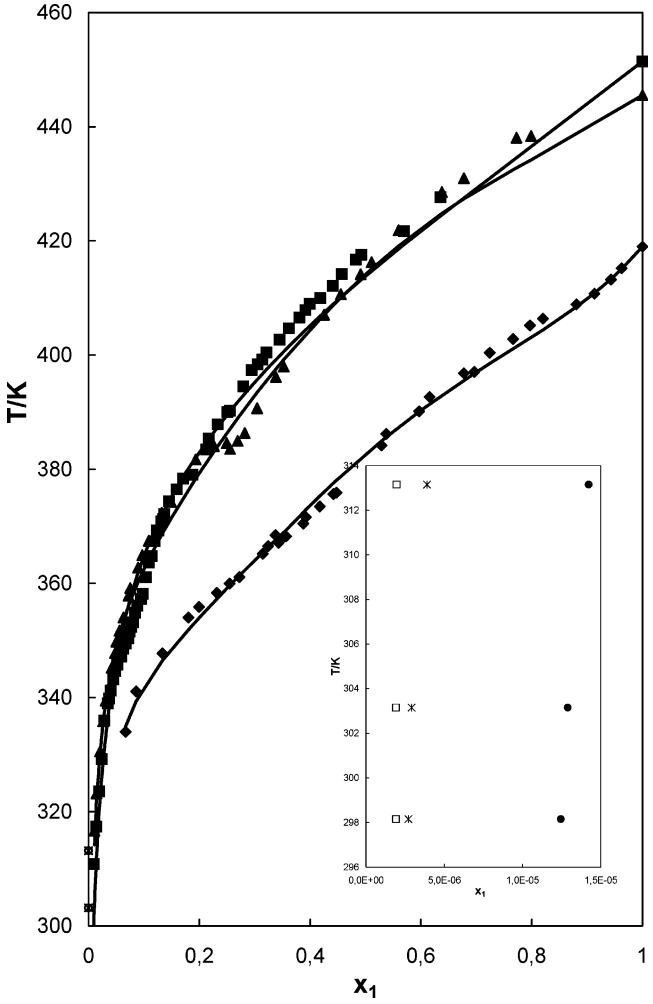


Figure 8. Solubility of (●) 1*H*-imidazole, (◆) 2-methyl-1*H*-imidazole, (▲) benzimidazole, (■) 2-methylbenzimidazole, (∗) 2-phenylimidazole, or (○) 4,5-diphenylimidazole in 2-nitrotoluene; points are the experimental values.

the oxygen from the nitro group and with the oxygen from the carbonyl group in ketones are similar.

The globular shape of 2,4,5TPhI, the spherical hindrance, the high fusion temperature, and the high enthalpy of melting cause this compound to solubilize with different aggregates of the solute in the solvent. It was shown previously that 2,4,5TPhI, in comparison with other imidazoles, does not affect the surface tension.[3] The results of solubility in this work differ from expectations. The solubility of the imidazoles under study decreases in different organic solvents in the order: phenylimidazoles < benzimidazoles < 2-methyl-1*H*-imidazole < 1*H*-imidazole.

The correlation of the experimental curves (only for the synthetic method) is worse than that for solubilities in alcohols because the solubilities observed are much lower.

Our results, obtained with imidazoles, may be useful for predicting physical and phase properties of ionic liquids, synthesized on the base of an imidazole molecule.

Acknowledgment

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