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Solubility of Imidazoles in Ethers

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Solid−liquid equilibrium (SLE) has been measured from 270 K to the melting temperature of the solid for 15 binary mixtures of an imidazole (1*H*-imidazole, 2-methyl-1*H*-imidazole, and 1,2-dimethylimidazole) with ethers [dipropyl ether, dibutyl ether, dipentyl ether, methyl 1,1-dimethylethyl ether (*tert*-butyl methyl ether), and methyl 1,1-dimethylpropyl ether (*tert*-amyl methyl ether)] using a dynamic method. The solubility of imidazoles in ethers is lower than that in alcohols and in water and generally decreases with increasing of the ether chain length. Additionally, two liquid phases were observed for mixtures of 1*H*-imidazole and 1,2-dimethylimidazole in dibutyl ether and dipentyl ether. The intermolecular solute−solvent interaction is higher for branch chain ethers, and the mutual solubility is much higher, which results in one liquid phase being observed. Experimental results of solubility are compared with values calculated by means of the Wilson, UNIQUAC, and NRTL equations utilizing parameters derived from SLE results. The existence of a solid−solid first-order phase transition in 2-methyl-1*H*-imidazole has been observed and has been taken into consideration in the solubility calculation. The best correlation of the solubility data was obtained with the Wilson equation.

Introduction

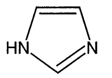
The use of imidazoles and their derivatives in chemical processes is becoming increasingly important. Their ability to partake in hydrogen bond formation is widely used in the production of pharmaceuticals.[1,2]

A new class of low melting *N*,*N*′-dialkylimidazolium salts are presently known as some of the most inert and least nucleophilic anions.[3,4] The packing inefficiency of the *N*,*N*′-dialkylimidazolium salts and the asymmetry of the cation are the major reasons for their low melting temperatures.[5] 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. The first measurements of the liquid−liquid equilibria (LLE) of [Bmim][PF$_6$] with selected organic solvents were presented already.[6]

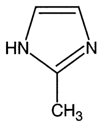
We have begun a systematic investigation into the thermodynamic properties and phase equilibria of simple imidazole molecules and the new class of their ionic salts.[7−10] The densities, surface tensions, octanol/water partition coefficients, and solid−liquid and liquid−liquid equilibria of many binary mixtures are under investigation. The purpose of this paper is to report the solubility of three imidazoles (1*H*-imidazole, 2-methyl-1*H*-imidazole, and 1,2-dimethylimidazole) with ethers (dipropyl ether, dibutyl ether, dipentyl ether, methyl 1,1-dimethylethyl ether, and methyl 1,1-dimethylpropyl ether) using a dynamic method.

The molecular structures of the imidazoles under study are shown below.

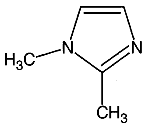
1***H***-Imidazole



2-Methyl-1***H***-imidazole



1,2-Dimethylimidazole



Experimental Section

The origins of the chemicals (Chemical Abstracts Service Registry Numbers as provided by the author are given in parantheses) and their mass percent purities are as follows: dipropyl ether (111-43-3, Aldrich, >99%), dibutyl ether (142-96-1, Aldrich, >99%), dipentyl ether (693-65-2, Fluka AG, >99%), methyl 1,1-dimethylethyl ether (1634-04-46, Aldrich, 99.5+%), methyl 1,1-dimethylpropyl ether (994-05-8, Aldrich, >99%), 1*H*-imidazole (288-32-4, Koch-Light Lab., 99%), 2-methyl-1*H*-imidazole (693-98-1, Koch-Light Lab., 99%), 1,2-dimethylimidazole (1739-84-0, Koch Light Lab., 98%). All solvents were fractionally distilled over different drying reagents to a mass fraction purity better than 99.8%. Liquids were stored over freshly activated molecular sieves of type 4A (Union Carbide). 1*H*-Imidazole was used immediately after fractional distillation under reduced pressure, because it is a very hygroscopic substance. All compounds were checked by GLC analysis (detection limit 0.01%), and no significant impurities were found. Analysis, using the Karl-Fischer technique, showed that the water content in each of the solvents was less than 0.02 mol %. Physical properties of the pure imidazoles are collected in Table 1.

Solid−liquid equilibrium temperatures were determined using a dynamic method described in detail previously.[12] 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 P550 (DOSTMANN Electronic GmbH) with the probe totally 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 reproducibility of measurements was δT/K =

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Table 1. Physical Constants of Pure Compounds: T_m, Melting Temperatures (This Work); ΔH_m, Molar Enthalpy of Fusion; $\Delta C_{p,m}$, Heat Capacity Change at the Melting Temperature; and $V^{298.15}$, Molar Volume

component	T_m / K	T_{tr}[a] / K	ΔH_m[a] / kJ·mol^{-1}	ΔH_{tr}[a] / kJ·mol^{-1}	$\Delta C_{p,m}$[a] / J·K^{-1}·mol^{-1}	$V^{298.15}$ [a] / cm^3·mol^{-1}
1*H*-imidazole	362.25[b]		12.82[b]		24.17	61.6
2-methyl-1*H*-imidazole	419.00	366.85	12.67	1.59	41.05	76.1
1,2-dimethylimidazole	311.50		7.93		12.00	96.1

[a] From ref 8. [b] The literature value[11] of the melting temperature is 362.69 K, and the enthalpy of melting is 12.82 kJ·mol^{-1}.

0.1 and $\delta x_1 = 0.0005$. The estimated uncertainties in the reported activity coefficients were $\delta\gamma_1 = 0.1$.

Results and Discussion

The solubility of a solid 1 in a liquid may be expressed in a very general manner by eq 1

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

where x_1, γ_1, ΔH_{m1}, $\Delta C_{p,m1}$, T_{m1}, and T stand for mole fraction, activity coefficient, enthalpy of fusion, difference in solute heat capacity between the solid and liquid at the melting temperature, melting temperature of the solute (1), and equilibrium temperature, respectively.

If a solid−solid transition occurs before fusion (2-methyl-1*H*-imidazole), an additional term must be added to the right-hand side of eq 1.[13,14] 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

$$-\ln x_1 = \frac{\Delta H_{m1}}{R}\left(\frac{1}{T} - \frac{1}{T_{m1}}\right) + \frac{\Delta H_{tr1}}{R}\left(\frac{1}{T} - \frac{1}{T_{tr1}}\right) - \frac{\Delta C_{p,m1}}{R}\left(\ln \frac{T}{T_{m1}} + \frac{T_{m1}}{T} - 1\right) + \ln \gamma_1 \quad (2)$$

where ΔH_{tr1} and T_{tr1} stand for the enthalpy of the transition and the transition temperature of the solute, respectively.

In this study three methods were used to derive the solute activity coefficients, γ_1, from the following three correlation equations for G^E: the Wilson,[15] UNIQUAC,[16] and NRTL equation.[17] The exact mathematical forms of the equations have been presented in our previous paper.[18]

The parameters of the equations were found by an optimization technique:[19]

$$\Omega = \sum_{i=1}^{n} [T_i^{exp} - T_i^{cal}(x_{1i},P_1,P_2)]^2 \quad (3)$$

where Ω is the objective function, n is the number of experimental points, and T_i^{exp} and T_i^{cal} denote respectively the experimental and calculated equilibrium temperature corresponding to the concentration x_{1i}. P_1 and P_2 are model parameters resulting from the minimization procedure, obtained by solving the nonlinear equation (eq 1 or 2), depending upon the value of temperature and the expression for the logarithm of the activity according to the assumed model. The root-mean-square deviation of temperature was defined as follows:

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

Table 2. Molar Volume, V_m, for Ethers

ether	V_m(298.15 K)/cm^3·mol^{-1}
dipropyl	137.7[a]
dibutyl	170.4[a]
dipentyl	203.2[a]
methyl 1,1-dimethylethyl ether	119.9[b]
methyl 1,1-dimethylpropyl ether	133.4[b]

[a] From ref 21. [b] From ref 22.

Table 3. Experimental Solid−Liquid Equilibrium Temperatures, T, for {1*H*-Imidazole (1) + an Ether (2)} Systems, and γ_1, the Experimental Activity Coefficient of the Solute

x_1	T/K	γ_1	x_1	T/K	γ_1	x_1	T/K	γ_1
Dipropyl Ether								
0.1048	290.36	3.6	0.3907	327.57	1.6	0.7517	348.50	1.1
0.1464	300.07	3.0	0.4110	328.70	1.6	0.8297	353.56	1.1
0.1901	309.33	2.6	0.4869	332.89	1.4	0.8873	357.75	1.1
0.1984	310.60	2.6	0.5477	335.47	1.3	0.9489	360.01	1.0
0.2420	316.30	2.3	0.5977	338.50	1.2	1.0000	362.25	1.0
0.2991	321.70	2.0	0.6230	340.45	1.2			
0.3162	322.89	1.9	0.6838	346.10	1.2			
Dibutyl Ether								
0.0196	322.65	30.9	0.1950	348.02	4.3	0.7125	350.07	1.2
0.0288	328.25	22.7	0.2331	348.41	3.6	0.7837	350.74	1.1
0.0361	338.69	20.7	0.3027	348.85	2.8	0.8289	352.74	1.1
0.0530	342.63	14.8	0.3398	349.10	2.5	0.8707	354.71	1.0
0.0854	346.12	9.6	0.3726	349.21	2.3	0.9011	356.10	1.0
0.0868	346.15	9.5	0.5155	349.37	1.7	0.9301	357.72	1.0
0.1122	346.60	7.4	0.5660	349.31	1.5	0.9678	359.61	1.0
0.1389	347.21	6.0	0.6121	349.61	1.4	1.0000	362.25	1.0
0.1638	347.69	5.1	0.6624	349.66	1.3			
Dipentyl Ether								
0.0252	341.95	31.0	0.1554	351.55	5.7	0.6424	354.25	1.4
0.0299	343.45	26.6	0.2366	352.48	3.8	0.7398	354.37	1.2
0.0344	344.15	23.3	0.2769	352.42	3.2	0.8000	354.31	1.1
0.0409	346.22	20.1	0.3291	352.68	2.7	0.8447	354.40	1.1
0.0477	347.85	17.6	0.3580	352.90	2.5	0.8865	355.18	1.0
0.0611	348.29	13.8	0.3861	353.06	2.3	0.9186	356.40	1.0
0.0760	349.36	11.3	0.4169	353.09	2.1	0.9507	357.99	1.0
0.0925	350.07	9.3	0.4573	353.25	2.0	0.9580	359.25	1.0
0.1067	350.52	8.1	0.5036	353.62	1.8	0.9811	360.27	1.0
0.1336	351.20	6.5	0.5884	353.76	1.5	1.0000	362.25	1.0
Methyl 1,1-Dimethylethyl Ether								
0.0568	316.25	9.7	0.1214	321.87	4.9	0.3173	327.59	2.0
0.0820	318.72	7.0	0.1702	324.70	3.7	1.0000	362.25	1.0
Methyl 1,1-Dimethylpropyl Ether								
0.0404	321.91	14.8	0.3302	334.21	2.1	0.6745	348.37	1.2
0.0529	323.91	11.6	0.3807	335.27	1.9	0.7586	352.30	1.2
0.0723	326.34	8.8	0.4330	336.69	1.7	0.8559	357.58	1.1
0.1091	328.33	6.0	0.4770	338.47	1.6	0.9145	359.69	1.1
0.1548	329.99	4.3	0.5411	340.67	1.4	0.9245	359.84	1.0
0.2183	331.66	3.1	0.6117	344.86	1.3	1.0000	362.25	1.0

where T^{exp} and T^{cal}, respectively, are the experimental and calculated temperatures of the *i*th point, n is the number of experimental points (including the melting temperature), and 2 is the number of adjustable parameters.

The pure component structural parameters r (volume parameter) and q (surface parameter) in the UNIQUAC and NRTL equations were obtained by means of the following simple relationships:[20]

Table 4. Experimental Solid−Liquid Equilibrium Temperatures, *T* (Phases α and *β*, Respectively), for {2-Methyl-1*H*-imidazole (1) + an Ether (2)} Systems, and γ_1, the Experimental Activity Coefficient of the Solute

x_1	T_α or T_β/K	γ_1	x_1	T_α or T_β/K	γ_1	x_1	T_α or T_β/K	γ_1
				Dipropyl Ether				
0.0017	290.43(β)	149.3	0.0057	321.61(β)	65.5	0.0216	352.83(β)	24.8
0.0022	305.64(β)	139.7	0.0064	324.89(β)	60.6	0.0251	354.41(β)	21.9
0.0029	310.04(β)	111.9	0.0073	327.28(β)	54.7	0.0277	355.63(β)	20.4
0.0035	312.43(β)	95.4	0.0094	332.23(β)	45.0	0.0302	356.87(β)	19.3
0.0041	314.81(β)	83.9	0.0148	344.60(β)	32.9	1.0000	419.00(α)	1.0
0.0048	319.26(β)	75.6	0.0183	349.19(β)	28.1			
				Dibutyl Ether				
0.0012	278.61(β)	181.4	0.0182	354.33(β)	29.9	0.2839	386.69(α)	2.6
0.0015	286.25(β)	160.3	0.0212	357.13(β)	26.5	0.3179	387.04(α)	2.4
0.0018	292.48(β)	144.7	0.0250	360.09(β)	23.2	0.3582	388.04(α)	2.1
0.0021	297.46(β)	132.1	0.0281	362.37(β)	21.1	0.3993	388.72(α)	1.9
0.0023	301.71(β)	127.2	0.0309	364.28(β)	19.6	0.4408	390.31(α)	1.8
0.0027	306.14(β)	114.5	0.0328	365.63(β)	18.8	0.4824	391.77(α)	1.6
0.0030	310.01(β)	108.1	0.0342	366.79(β)	18.2	0.5214	392.72(α)	1.5
0.0032	312.52(β)	104.5	0.0364	367.33(α)	17.2	0.5568	394.08(α)	1.4
0.0037	320.84(β)	99.9	0.0380	368.28(α)	16.6	0.5888	394.93(α)	1.4
0.0042	323.35(β)	90.7	0.0389	368.96(α)	16.4	0.6214	396.31(α)	1.3
0.0047	324.32(β)	82.0	0.0587	371.53(α)	11.1	0.6500	397.23(α)	1.3
0.0052	327.45(β)	76.9	0.0796	374.11(α)	8.4	0.6803	397.60(α)	1.2
0.0061	331.56(β)	68.8	0.0995	376.98(α)	6.9	0.7059	398.03(α)	1.2
0.0072	336.40(β)	61.6	0.1227	379.65(α)	5.7	0.7328	400.41(α)	1.2
0.0088	340.96(β)	53.7	0.1454	381.23(α)	4.8	0.7717	401.68(α)	1.1
0.0104	340.20(β)	44.6	0.1676	382.12(α)	4.3	0.8021	404.24(α)	1.1
0.0118	343.03(β)	40.6	0.1915	383.20(α)	3.8	0.8394	406.79(α)	1.0
0.0135	347.95(β)	37.5	0.2227	384.52(α)	3.3	0.8725	410.72(α)	1.0
0.0156	351.63(β)	33.8	0.2494	385.60(α)	3.0	1.0000	419.00(α)	1.0
				Dipentyl Ether				
0.0024	321.49(β)	155.2	0.2142	392.53(α)	3.7	0.6126	398.13(α)	1.4
0.0033	329.20(β)	123.7	0.2363	392.73(α)	3.3	0.6304	398.42(α)	1.3
0.0044	337.77(β)	102.5	0.2481	392.86(α)	3.2	0.6480	398.60(α)	1.3
0.0056	342.55(β)	85.1	0.2694	393.03(α)	2.9	0.6827	399.22(α)	1.2
0.0068	345.64(β)	72.6	0.2920	393.13(α)	2.7	0.7007	399.81(α)	1.2
0.0082	349.34(β)	62.7	0.3128	393.60(α)	2.5	0.7206	400.67(α)	1.2
0.0092	351.43(β)	57.2	0.3316	393.93(α)	2.4	0.7401	401.38(α)	1.2
0.0102	355.34(β)	53.9	0.3532	394.67(α)	2.3	0.7583	402.19(α)	1.1
0.0136	361.90(β)	43.5	0.3744	394.81(α)	2.2	0.7677	402.57(α)	1.1
0.0185	367.03(α)	33.8	0.3943	395.09(α)	2.0	0.7964	404.02(α)	1.1
0.0237	371.93(α)	27.6	0.4287	395.87(α)	1.9	0.8186	405.40(α)	1.1
0.0314	375.30(α)	21.5	0.4492	396.24(α)	1.8	0.8369	406.36(α)	1.1
0.0391	378.00(α)	17.7	0.4682	396.59(α)	1.7	0.8541	407.63(α)	1.0
0.0493	380.61(α)	14.4	0.4864	397.13(α)	1.7	0.8761	409.12(α)	1.0
0.0764	386.02(α)	9.8	0.5043	397.21(α)	1.6	0.9111	411.78(α)	1.0
0.0920	387.99(α)	8.2	0.5231	397.48(α)	1.6	0.9305	413.13(α)	1.0
0.1093	388.97(α)	7.0	0.5336	397.82(α)	1.5	0.9514	414.87(α)	1.0
0.1247	389.76(α)	6.2	0.5641	398.08(α)	1.5	0.9718	416.24(α)	1.0
0.1643	391.42(α)	4.8	0.5806	398.09(α)	1.3	0.9847	417.51(α)	1.0
0.1813	391.94(α)	4.3	0.5972	398.12(α)	1.4	1.0000	419.00(α)	1.0
				Methyl 1,1-Dimethylethyl Ether				
0.0025	281.84(β)	90.8	0.0047	301.90(β)	62.4	0.0081	315.57(β)	42.8
0.0030	287.07(β)	81.0	0.0057	307.63(β)	55.3	0.0100	320.18(β)	36.7
0.0038	296.06(β)	71.7	0.0067	310.83(β)	48.9	1.0000	419.00(α)	1.0
				Methyl 1,1-Dimethylpropyl Ether				
0.0018	281.30(β)	125.3	0.0079	317.33(β)	44.9	0.035	348.43(β)	14.3
0.0024	289.56(β)	104.6	0.0102	325.02(β)	38.1	0.041	350.56(β)	12.5
0.0028	294.64(β)	95.6	0.0132	330.06(β)	31.2	0.047	352.45(β)	11.4
0.0040	302.10(β)	73.5	0.0170	335.01(β)	25.7	0.050	353.58(β)	10.7
0.0051	308.34(β)	62.3	0.0231	341.98(β)	20.5	1.000	419.00(α)	1.0
0.0064	312.50(β)	52.2	0.0294	345.80(β)	16.8			

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

$$q_i = \frac{(Z-2)r_i}{Z} + \frac{2(1-l_{\mathrm{i}})}{Z} \tag{6}$$

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 use the molar volumes of ethers presented in Table 2. It was shown[17] that a proper value of α_{12} can be specified a priori, with its value depending on the binary system. If α_{12} is assigned, the NRTL equation has two adjustable parameters per binary: Δu_{12} and Δu_{21}. In this work, for (imidazole + an ether) mixtures, the parameter α_{12}, a constant of proportionality similar to the nonrandomness constant of the NRTL equation ($\alpha_{12} = \alpha_{21} = 0.4$ or 0.5), was taken into account.

Tables 3−6 list the direct experimental results of the SLE or LLE temperatures, *T*, versus x_1, the mole fraction of the imidazoles, and γ_1, the experimental activity coefficients in saturated solution for the investigated systems.

Table 5. Experimental Solid–Liquid Equilibrium Temperatures, T, and Liquid–Liquid Equilibrium Temperatures, T_{LLE}, for {1,2-Dimethylimidazole (1) + an Ether (2)} Systems, and γ_1, the Experimental Activity Coefficient of the Solute

x_1	T/K	T_{LLE}/K	γ_1	x_1	T/K	T_{LLE}/K	γ_1	x_1	T/K	T_{LLE}/K	γ_1
				Dipropyl Ether							
0.3112	274.62		2.2	0.5539	290.24		1.4	0.7760	300.05		1.1
0.3602	277.38		1.9	0.5789	291.29		1.4	0.8081	301.39		1.1
0.3948	279.87		1.8	0.6128	293.01		1.3	0.8463	303.08		1.1
0.4220	281.96		1.7	0.6492	294.27		1.3	0.9032	306.31		1.0
0.4615	284.80		1.6	0.6908	296.20		1.2	0.9473	309.11		1.0
0.4934	286.63		1.6	0.7117	297.33		1.2	1.0000	311.50		1.0
0.5231	288.57		1.5	0.7431	298.76		1.2				
				Dibutyl Ether							
0.1521	290.63		5.2	0.3555	303.17	307.77	2.6	0.6150	303.17	303.35	1.5
0.1809	292.65		4.5	0.3907	303.17	307.18	2.3	0.6675	303.17	303.27	1.4
0.2052	294.65		4.1	0.4392	303.17	306.42	2.1	0.7342	303.83		1.3
0.2410	298.23		3.6	0.4853	303.17	305.31	1.9	0.7889	304.37		1.2
0.2823	303.17	305.40	3.3	0.5288	303.17	304.23	1.7	0.8690	306.04		1.1
0.3221	303.17	307.33	2.8	0.5687	303.17	303.44	1.6	1.0000	311.50		1.0
				Dipentyl Ether							
0.0701	280.77		10.3	0.4052	307.49	312.52	2.4	0.7000	307.49	313.01	1.4
0.1452	289.80		5.5	0.4321	307.49	313.04	2.2	0.7462	307.49	312.24	1.3
0.1989	295.75		4.3	0.4559	307.49	313.31	2.1	0.8028	307.49	310.24	1.2
0.2562	301.60		3.5	0.4909	307.49	313.98	2.0	0.8620	308.34		1.1
0.3021	307.49	307.01	3.2	0.5340	307.49	314.10	1.8	0.9265	309.72		1.1
0.3198	307.49	308.43	3.0	0.5622	307.49	314.01	1.7	0.9741	310.65		1.0
0.3457	307.49	310.18	2.8	0.6056	307.49	313.80	1.6	1.0000	311.50		1.0
0.3780	307.49	311.57	2.5	0.6487	307.49	313.40	1.5				
				Methyl 1,1-Dimethylethyl Ether							
0.1462	277.04		4.7	0.4450	292.37		1.8	0.8482	303.21		1.1
0.2008	281.97		3.6	0.5319	294.34		1.6	0.9401	307.26		1.0
0.2661	286.35		2.9	0.5957	295.68		1.4	1.0000	311.50		1.0
0.3314	289.41		2.4	0.6574	297.24		1.3				
0.4018	291.22		2.0	0.7540	300.56		1.2				
				Methyl 1,1-Dimethylpropyl Ether							
0.1700	281.13		4.3	0.3602	291.12		2.2	0.7222	300.44		1.2
0.1991	283.12		3.7	0.4218	292.69		1.9	0.7898	302.81		1.2
0.2357	285.36		3.2	0.4699	293.57		1.8	0.8603	304.95		1.1
0.2736	287.79		2.8	0.5310	295.11		1.6	0.9308	307.75		1.0
0.3142	289.67		2.5	0.6091	297.25		1.4	1.0000	311.50		1.0

Table 6. Experimental Liquid–Liquid Equilibrium Temperatures, T_{LLE}, for {1*H*-Imidazole (1) + an Ether (2)} Systems

x_1	T_{LLE}/K	x_1	T_{LLE}/K	x_1	T_{LLE}/K
		Dibutyl Ether			
0.5532	415.03	0.6320	386.82	0.6624	349.70
0.5842	410.35	0.6480	376.05		
0.6108	400.95	0.6495	362.20		
		Dipentyl Ether			
0.7050	462.25	0.7450	436.10	0.8193	381.00
0.7205	455.05	0.7852	416.50		
0.7372	445.05	0.7984	400.15		

The solid–liquid and liquid–liquid equilibria curves are shown as an example for 1,2-dimethylimidazole (1) in ethers (2) in Figure 1.

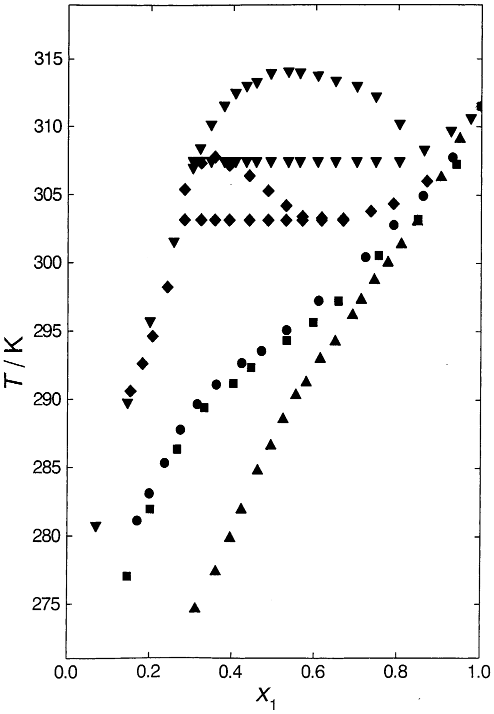

Figure 1. Solubility of 1,2-dimethylimidazole (1) in- ▲, dipropyl ether, ■, methyl 1,1-dimethylethyl ether, ●, methyl 1,1-dimethylpropyl ether, ◆,dibutyl ether, and ▼, dipentyl ether.

Experimental phase diagrams of SLE investigated in this work are characterized mainly by the following: (i) Positive deviations from ideality were found for every mixture. Thus, the solubility is lower than the ideal one; $\gamma_1 > 1$ (see the values of activity coefficients in Tables 3–5 and Figure 2 for the three imidazoles). (ii) The solubility of the imidazoles was highest in dipropyl ether and the two branch chain ethers. (iii) The solubilities of 1*H*-imidazole and 1,2-dimethylimidazole in dibutyl ether and dipentyl ether are very low, and as it is shown in Tables 5 and 6, a miscibility gap was observed for these four mixtures (see Figures 1 and 2). The mutual solubility is higher for the 1,2-dimethylimidazole than that of 1*H*-imidazole in ether and is higher for certain imidazoles in dibutyl ether than in dipentyl ether. The coexistence curve is shifted to lower mole fraction of the solute, x_1, in dibutyl ether. The critical temperatures and compositions were possible to obtain experimentally only for the 1,2-dimethylimidazole (T_c =

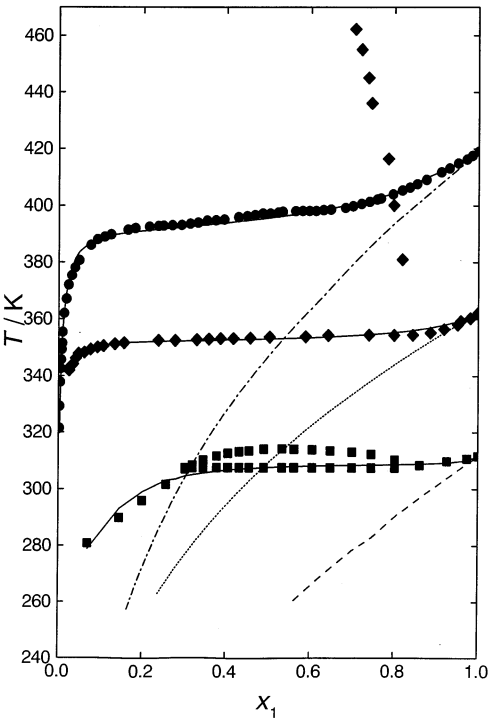

Figure 2. Solubility of ◆, 1*H*-imidazole (1), or ●, 2-methyl-1*H*-imidazole (1), or ■, 1,2-dimethylimidazole (1) in dipentyl ether. Solid lines are from calculations by the NRTL equation (1*H*-imidazole and 1,2-dimethylimidazole) and by the Wilson equation (2-methyl-1*H*-imidazole); dotted lines designate ideal solubility.

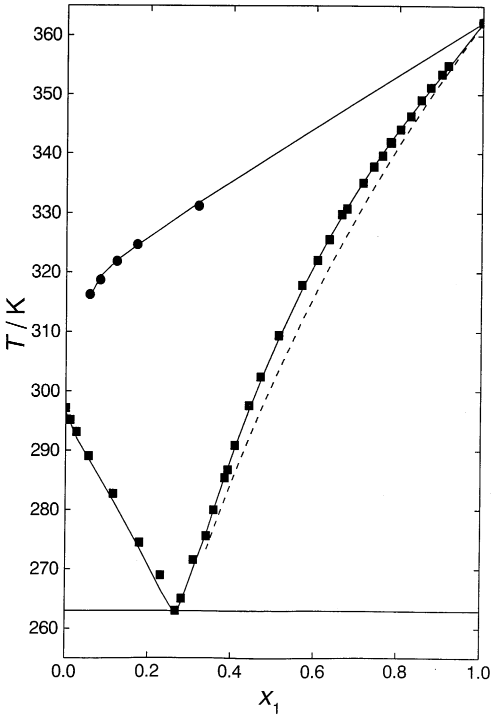

Figure 3. Comparison between solubilities of 1*H*-imidazole (1) in ●, methyl 1,1-dimethylpropyl ether, or ■, *tert*-butyl alcohol. Solid lines, calculated by the Wilson equation; dotted line designates ideal solubility.

307.8 K for $x_{1c} = 0.355$ and $T_c = 314.1$ K for $x_{1c} = 0.534$ in the dibutyl and dipentyl ether, respectively). The critical temperature increases with increase in the number of carbon atoms of the ether molecule. For 1*H*-imidazole a miscibility gap is shifted to the very low concentration of

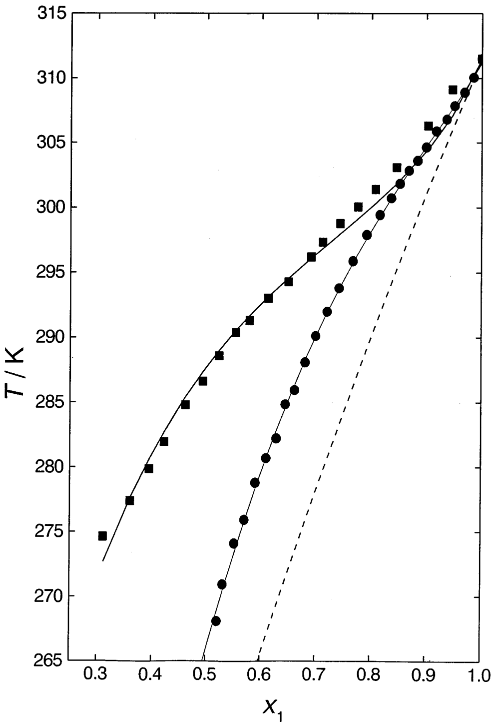

Figure 4. Comparison between solubilities of 1,2-dimethylimidazole (1) in ●, 1-hexanol, or ■, dipropyl ether. Solid lines are from calculations by the Wilson equation; dotted line designates ideal solubility.

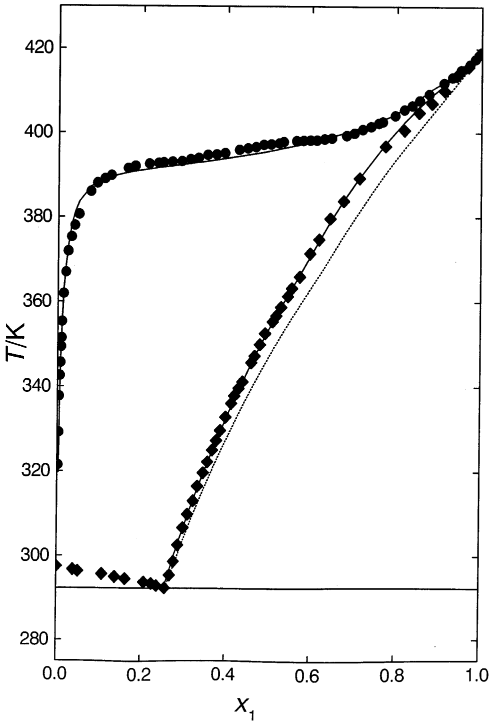

Figure 5. Comparison between solubilities of 2-methyl-1*H*-imidazole (1) in ●, dipentyl ether, or in ◆, 1-dodecanol. Solid lines are from calculations by the Wilson equation; dotted line designates ideal solubility.

solute; thus, the second liquid–liquid equilibrium temperatures may be possible to observe only by special techniques. 2-Methyl-1*H*-imidazole exhibits complete miscibility with all systems in the liquid phase. (iv) It was observed that the solubilities of imidazoles in ethers are lower than those in alcohols.[7] The comparisons are shown in Figures

Table 7. Correlation of the Solubility Data (SLE) of {Imidazole (1) + an Ether (2)} by Means of the Wilson, UNIQUAC, and NRTL Equations: Values of Parameters and Measures of Deviations

	parameters			deviations		
	Wilson $g_{12}-g_{11}$ $g_{12}-g_{22}$	UNIQUAC Δu_{12} Δu_{21}	NRTL[a] Δg_{12} Δg_{21}	Wilson σ[b]	UNIQUAC σ[b]	NRTL σ[b]
solvent	$\mathrm{J\cdot mol^{-1}}$	$\mathrm{J\cdot mol^{-1}}$	$\mathrm{J\cdot mol^{-1}}$	K	K	K
1*H*-Imidazole						
dipropyl ether	4635.17	−610.92	2448.56	1.51	1.63	1.60
	278.66	3855.49	2534.98			
dibutyl ether		−850.77	3755.61[c]		4.12	3.52[c]
		8522.69	7573.93[c]			
dipentyl ether		−882.33	4424.65		5.81	4.86
		9151.83	8157.05			
methyl 1,1-dimethylethyl ether	10688.79	−1133.58	2368.10[c]	0.65	1.73	1.28[c]
	−56.53	7378.68	6646.94[c]			
methyl 1,1-dimethylpropyl ether	11186.33	−925.53	3581.87[c]	2.60	4.62	2.58[c]
	416.80	7412.81	7170.05[c]			
2-Methyl-1*H*-imidazoledipropyl ether						
dipropyl ether	13233.07		−783.87	2.65		4.13
	509.85		13274.21			
dibutyl ether	13370.12	−1559.97	5225.15[c]	2.21	12.55	6.93[c]
	908.62	8889.80	10029.45[c]			
dipentyl ether	14953.45	−1397.15	6622.63[c]	1.28	11.59	7.14[c]
	1267.49	8875.49	10664.02[c]			
methyl 1,1-dimethylethyl ether	11302.48		230.62	1.17		1.00
	638.85		10970.50			
methyl 1,1-dimethylpropyl ether	12466.14	−2238.47	−640.27	1.06	5.18	3.62
	−57.97	107331.30	11998.84			
1,2-Dimethylimidazole						
dipropyl ether	1916.13	1125.54	4112.23	1.00	1.36	1.39
	3432.24	304.45	732.97			
dibutyl ether		147.15	5084.04		1.96	1.18
		2301.13	3696.46			
dipentyl ether		−105.98	5812.11		4.08	2.83
		2794.55	4160.87			
methyl 1,1-dimethylethyl ether	4447.03	487.23	3502.19	0.77	2.23	1.61
	3426.68	1652.97	3217.83			
methyl 1,1-dimethylpropyl ether	4686.37	346.22	4542.91	1.18	2.52	0.89
	3445.94	1763.50	4479.43			

[a] Calculated with the third nonrandomness parameter $\alpha = 0.4$. [b] According to eq 4 in the text. [c] Calculated with the third nonrandomness parameter $\alpha = 0.5$.

3−5 for 1*H*-imidazole in methyl 1,1-dimethylpropyl ether and 2-methyl-2-propanol (*tert*-butyl alcohol), for 1,2-dimethylimidazole in dipropyl ether and 1-hexanol, and for 2-methyl-1*H*-imidazole in dipenthyl ether and 1-dodecanol. (v) The simple eutectic systems are expected to represent mixtures under study following the (imidazole + an alcohol) binary mixtures[7] that are presented in Figures 3 and 5. The eutectic points are $x_{1,\mathrm{e}} = 0.26 \pm 0.001$, $T_\mathrm{e}/\mathrm{K} = 263.05 \pm 0.1$ and $x_{1,\mathrm{e}} = 0.26 \pm 0.02$, $T_\mathrm{e}/\mathrm{K} = 292.35 \pm 0.1$ for 1*H*-imidazole and 2-methyl-1*H*-imidazole in 1-dodecanol.

Equations 1 and 2 were used in the correlations of the experimental points with the assumption that the mixtures under study are simple eutectic systems. Table 7 lists the results of fitting the solubility curves by the three equations used: Wilson, UNIQUAC, and NRTL. For the mixtures showing liquid−liquid equilibria, the Wilson equation was omitted.

For the 15 systems presented in this work the best description of solid−liquid equilibrium was given by the two-parameter Wilson equation. The results of correlations of imidazole by use of UNIQUAC and NRTL gave much worse deviations, and the calculated curves do not represent the possible shape of the liquidus curve between the experimental points and the melting temperature, especially when the experimental points are only in a very narrow solute mole fraction range (i.e. 2-methyl-1*H*-imidazole in dipropyl ether or methyl 1,1-dimethylethyl ether).

Conclusions

The solubility of 1*H*-imidazole and 2-methyl-1*H*-imidazole in ethers decreases with an increase in molecular weight of an ether, but in the branch chain ethers the solubility is much higher than that in longer chain ethers. The solubility of 2-methyl-1*H*-imidazole in ethers shows different solute−solvent interactions; the substitution of the methyl group in position 2 of the imidazole ring increases the mutual solubility. As a result, a miscibility gap is not observed for the 2-methyl-1*H*-imidazole in dibutyl and dipentyl ether.

The best results correlation equation was the two-parameter Wilson equation with the rms deviation $\sigma = 1.46$ K.

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