Solubility of Imidazoles in Alcohols

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The solid−liquid equilibrium (SLE) has been measured from 270 K to the melting temperature of the solid for 24 binary mixtures of an imidazole (1*H*-imidazole, 2-methyl-1*H*-imidazole, and 1,2-dimethylimidazole) with an alcohol (ethanol, propan-1-ol, propan-2-ol, butan-1-ol, butan-2-ol, 2-methylpropan-2-ol, hexan-1-ol, and dodecan-1-ol) using a dynamic method. The melting point, enthalpy of fusion, and heat capacity change at the melting temperature were determined by differential scanning calorimetry. The solubility of imidazoles in alcohol is lower than in water and generally decreases with increasing molecular weight of the alcohol. The intermolecular solute−solvent interaction for 2,3-dimethylimidazole is higher for secondary and tertiary alcohols. Experimental results of solubility are compared with values calculated 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 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 has been obtained by the Wilson equation, by which the average root-mean-square deviation for three imidazoles is 0.89.

Introduction

The use of imidazoles and their derivatives in chemical processes is becoming increasingly important. Their potential for hydrogen bond formation is widely used in pharmaceuticals. Several ruthenium(III) complexes have been evaluated and used extensively in cancer therapy treatment.[1,2] 1*H*-Imidazole is normally used as an antimetabolite and as an inhibitor of histamine and also is used in many syntheses.

Molecules belonging to a new class of low-melting *N*,*N*′-dialkylimidazolium salts 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 of their low melting temperatures.[3] 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 stabilities. 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 density, viscosity, refractive index, and heat capacity, as well as the liquid−liquid equilibria of 1-butyl-3-methylimidazolium hexafluorophosphate with selected organic solvents, were presented recently.[4]

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. The densities, surface fractions, 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 alcohols (ethanol, propan-1-ol, propan-2-ol, butan-1-ol, butan-2-ol, 2-methylpropan-2-ol, hexan-1-ol, and dodecan-1-ol).

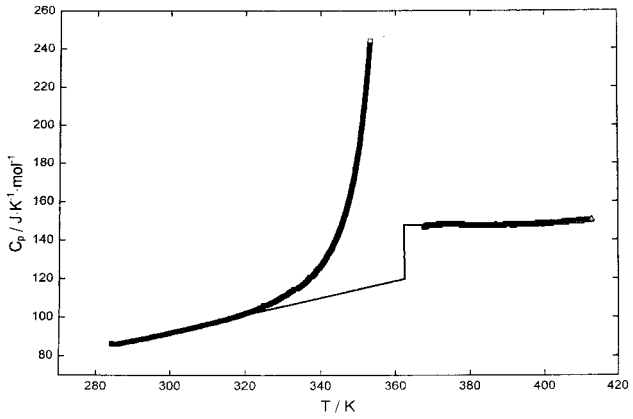
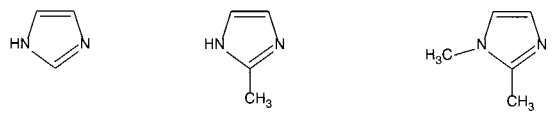


Figure 1. Molar heat capacity changing at the melting temperature, ΔC_p, of 1*H*-imidazole.

1-H-Imidazole 2-Methyl-1-H-imidazole 1,2-Dimethylimidazole



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

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10.1021/je0101303 CCC: $22.00
Published on Web 11/22/2001

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

component	T_m/K	T_{tr}/K	ΔH_m/kJ·mol^{-1}	ΔH_{tr}/kJ·mol^{-1}	ΔC_{pm}/J·K^{-1}·mol^{-1}	$V^{298.15\ K}$ [a]/cm^3·mol^{-1}
1*H*-imidazole	362.25[b]		11.18[b]		24.17	106.6
2-methyl-1*H*-imidazole	419.00	366.85	12.67	1.59	41.05	106.1
1,2-dimethylimidazole	311.50		7.93		12.00	126.1

[a] Calculated with group contribution to molar volume from Barton.[5] [b] The literature value[6] of the melting temperature is 362.69 K, and the enthalpy of melting is 12.82 kJ·mol^{-1}.

Table 2. Experimental Solid−Liquid Equilibrium Temperatures (T) for 1*H*-Imidazole (1) + Alcohol (2) Systems and γ_1 Experimental Activity Coefficients of Solute

x_1	T/K	γ_1	x_1	T/K	γ_1	x_1	T/K	γ_1	x_1	T/K	γ_1
					Ethanol						
0.3752	278.79	1.029	0.5160	305.47	1.016	0.6734	327.91	1.022	0.8954	351.34	1.000
0.4053	285.78	1.010	0.5406	309.06	1.015	0.7097	332.46	1.021	0.9521	356.25	1.000
0.4211	288.80	1.001	0.5575	311.82	1.018	0.7498	336.95	1.017	1.0000	362.25	1.000
0.4475	293.10	1.000	0.5931	317.53	1.026	0.7946	342.02	1.015			
0.4849	300.18	1.011	0.6178	320.66	1.023	0.8462	346.73	1.004			
0.4881	300.94	1.014	0.6337	323.04	1.026	0.8720	349.27	1.001			
					Propan-1-ol						
0.3737	277.24	1.000	0.5091	304.16	1.013	0.6980	330.40	1.014	0.8823	350.91	1.007
0.3835	279.63	1.000	0.5568	311.87	1.020	0.7396	335.17	1.011	0.9314	356.05	1.007
0.4287	289.35	1.000	0.6060	319.02	1.023	0.7846	340.43	1.010	0.9585	358.75	1.006
0.4662	297.22	1.012	0.6565	325.27	1.016	0.8281	345.47	1.012	1.0000	362.25	1.000
					Propan-2-ol						
0.3348	278.66	1.095	0.5235	311.51	1.080	0.6719	331.08	1.062	0.9674	358.61	1.000
0.3671	285.34	1.095	0.5457	314.71	1.078	0.7646	340.90	1.042	1.0000	362.25	1.000
0.4058	293.32	1.104	0.5879	320.43	1.072	0.8523	349.61	1.028			
0.4480	300.42	1.098	0.6156	323.85	1.066	0.8747	350.69	1.013			
0.4887	306.50	1.087	0.6685	330.04	1.055	0.9176	354.33	1.004			
					Butan-1-ol						
0.3331	275.17	1.046	0.5178	309.96	1.072	0.7280	336.41	1.041	0.9661	359.18	1.003
0.3889	288.72	1.083	0.5797	319.04	1.069	0.7818	341.93	1.031	0.9844	361.09	1.004
0.4220	295.45	1.092	0.6317	325.75	1.062	0.8334	346.87	1.021	1.0000	362.25	1.000
0.4565	300.38	1.077	0.6521	327.75	1.053	0.8849	351.72	1.012			
0.4825	305.65	1.085	0.6801	331.18	1.050	0.9380	356.63	1.006			
					Butan-2-ol						
0.3311	276.53	1.073	0.5062	309.82	1.094	0.6868	332.72	1.059	0.9442	358.65	1.020
0.3630	283.64	1.082	0.5363	313.83	1.085	0.7174	336.09	1.053	0.9613	360.25	1.019
0.3925	290.06	1.093	0.5639	318.02	1.086	0.8160	345.97	1.032	1.0000	362.25	1.000
0.4184	295.62	1.104	0.5907	321.17	1.076	0.8552	349.42	1.022			
0.4516	300.99	1.097	0.6199	324.54	1.067	0.8935	353.00	1.016			
0.4807	305.74	1.095	0.6549	328.78	1.061	0.9214	355.75	1.015			
					2-Methylpropan-2-ol						
0.0000	297.16		0.3092	271.63	1.028	0.5679	317.84	1.076	0.7820	341.80	1.029
0.0111	295.18		0.3396	275.65	1.033	0.6052	322.05	1.061	0.8038	344.06	1.026
0.0265	293.14		0.3572	280.02	1.045	0.6339	325.58	1.056	0.8283	346.34	1.021
0.0556	289.04		0.3834	285.43	1.050	0.6638	329.77	1.059	0.8534	349.06	1.020
0.1155	282.72		0.3909	286.77	1.049	0.6757	330.74	1.052	0.8760	351.18	1.017
0.1789	274.52		0.4079	290.92	1.064	0.7146	335.06	1.045	0.9020	353.47	1.012
0.2297	269.01		0.4414	297.57	1.074	0.7404	337.78	1.040	0.9174	354.91	1.010
0.2669	263.03		0.4686	302.44	1.077	0.7608	339.62	1.033	1.0000	362.25	1.000
0.2809	265.08	1.020	0.5123	309.38	1.075	0.7799	341.95	1.034			
					Hexan-1-ol						
0.3396	276.92	1.052	0.4903	306.05	1.078	0.7133	334.34	1.038	0.9373	356.30	1.003
0.3630	281.62	1.052	0.5204	310.29	1.071	0.7528	338.70	1.033	0.9705	358.95	1.000
0.3897	287.37	1.061	0.5556	315.47	1.068	0.7927	342.37	1.022	1.0000	362.25	1.000
0.4161	293.34	1.077	0.5945	320.86	1.065	0.8270	345.88	1.017			
0.4413	297.56	1.073	0.6366	325.82	1.055	0.8657	351.26	1.008			
0.4635	301.42	1.075	0.6772	330.43	1.046	0.9010	353.08	1.009			
					Dodecan-1-ol						
0.0000	297.50		0.2899	292.09		0.4705	318.69	1.312	0.7530	346.79	1.129
0.0983	295.97		0.3407	297.91	1.397	0.5146	324.75	1.289	0.8427	352.26	1.069
0.1351	295.35		0.3713	303.38	1.376	0.5591	330.02	1.261	0.8697	353.93	1.054
0.1591	294.85		0.3958	308.04	1.369	0.5968	333.94	1.235	0.9443	358.34	1.017
0.1835	294.35		0.4142	311.03	1.357	0.6409	338.23	1.207	0.9793	360.72	1.005
0.2335	293.32		0.4465	315.37	1.328	0.6992	342.60	1.161	1.0000	362.25	1.000

Experimental Section

The origins of the chemicals (Chemical Abstracts Service Registry Numbers as provided by the author are given in parentheses) and their mass percent purities are as follows: ethanol (64-17-5, Aldrich, spectrophotometric grade), propan-1-ol (71-23-8, POCH, Gliwice, >99%), propan-2-ol (67-63-0, POCH, Gliwice, HPLC grade), butan-1-ol (71-36-3, POCH, Gliwice, HPLC grade), butan-2-ol (78-92-2,

Table 3. Experimental Solid−Liquid Equilibrium Temperatures (T, Phases α and β, Respectively) for 2-Methyl-1*H*-imidazole (1) + Alcohol (2) Systems and γ_1 Experimental Activity Coefficients of 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	x_1	T_α or T_β/K	γ_1
					Ethanol						
0.2489	276.57(β)	0.851	0.3236	301.71(β)	0.905	0.4039	324.86(β)	0.960	1.0000	419.00(α)	1.000
0.2682	284.19(β)	0.873	0.3422	307.65(β)	0.921	0.4289	330.95(β)	0.972			
0.2874	290.38(β)	0.883	0.3607	312.56(β)	0.928	0.4570	338.46(β)	0.995			
0.3063	296.21(β)	0.892	0.3810	318.14(β)	0.940	0.4853	345.56(β)	1.000			
					Propan-1-ol						
0.2582	274.11(β)	0.794	0.3593	307.26(β)	0.873	0.4376	330.13(β)	0.943	0.5393	351.87(β)	0.981
0.2791	281.17(β)	0.807	0.3701	310.14(β)	0.878	0.4512	333.27(β)	0.949	0.5554	355.56(β)	0.993
0.2961	287.10(β)	0.821	0.3826	313.31(β)	0.883	0.4647	336.16(β)	0.953	0.5696	358.16(β)	0.996
0.3098	291.52(β)	0.831	0.3949	317.25(β)	0.897	0.4767	338.73(β)	0.957	0.5817	359.60(β)	0.991
0.3190	294.72(β)	0.840	0.4002	318.55(β)	0.899	0.4926	342.04(β)	0.962	0.5927	361.75(β)	0.996
0.3301	298.23(β)	0.849	0.4079	320.56(β)	0.903	0.5042	344.67(β)	0.968	0.6032	364.18(β)	1.000
0.3399	301.24(β)	0.856	0.4116	323.32(β)	0.925	0.5150	347.16(β)	0.961	1.0000	419.00(α)	1.000
0.3496	304.17(β)	0.863	0.4244	326.74(β)	0.935	0.5275	349.62(β)	0.978			
					Propan-2-ol						
0.2206	276.46(β)	0.959	0.2710	294.85(β)	0.991	0.3428	316.86(β)	1.028	0.4543	342.17(β)	1.044
0.2285	279.49(β)	0.964	0.2783	297.85(β)	1.002	0.3538	320.13(β)	1.036	0.4697	344.58(β)	1.038
0.2341	281.41(β)	0.965	0.2861	301.65(β)	1.022	0.3660	323.75(β)	1.046	0.4871	349.00(β)	1.052
0.2397	284.30(β)	0.978	0.2940	302.95(β)	1.011	0.3787	326.58(β)	1.045	0.5084	354.52(β)	1.072
0.2452	286.09(β)	0.979	0.3030	307.74(β)	1.041	0.3926	328.91(β)	1.036	1.0000	419.00(α)	1.000
0.2514	288.06(β)	0.979	0.3119	310.07(β)	1.041	0.4068	331.95(β)	1.036			
0.2580	290.25(β)	0.982	0.3208	311.72(β)	1.032	0.4214	335.25(β)	1.039			
0.2640	292.45(β)	0.987	0.3309	314.03(β)	1.029	0.4362	338.75(β)	1.046			
					Butan-1-ol						
0.2573	278.25(β)	0.846	0.3734	315.93(β)	0.936	0.4927	343.78(β)	0.982	0.6381	371.55(α)	1.022
0.2703	283.33(β)	0.861	0.3838	318.67(β)	0.941	0.5060	346.48(β)	0.985	0.6808	380.10(α)	1.037
0.2827	288.13(β)	0.875	0.3946	321.49(β)	0.946	0.5221	350.77(β)	1.002	0.6922	383.21(α)	1.050
0.2946	292.01(β)	0.883	0.4064	324.46(β)	0.952	0.5375	353.24(β)	1.000	0.7056	384.96(α)	1.047
0.3070	296.88(β)	0.901	0.4190	327.52(β)	0.957	0.5532	355.89(β)	1.001	0.7219	386.32(α)	1.041
0.3178	299.86(β)	0.903	0.4322	330.72(β)	0.963	0.5698	358.96(β)	1.005	0.7330	388.99(α)	1.045
0.3283	303.53(β)	0.915	0.4461	333.77(β)	0.967	0.5865	361.76(β)	1.007	1.0000	419.00(α)	1.000
0.3388	306.45(β)	0.919	0.4560	336.06(β)	0.972	0.5951	363.11(β)	1.007			
0.3496	309.68(β)	0.927	0.4679	338.72(β)	0.976	0.6092	365.43(β)	1.009			
0.3614	312.91(β)	0.932	0.4807	341.43(β)	0.979	0.6215	368.90(α)	1.024			
					Butan-2-ol						
0.2471	280.53(β)	0.903	0.3466	311.26(β)	0.950	0.4348	333.47(β)	0.987	0.5420	355.20(β)	1.013
0.2668	287.27(β)	0.913	0.3567	314.51(β)	0.961	0.4480	336.43(β)	0.991	0.5575	357.79(β)	1.014
0.2836	293.03(β)	0.925	0.3672	316.81(β)	0.959	0.4629	339.58(β)	0.995	0.5724	360.42(β)	1.016
0.2966	296.50(β)	0.924	0.3782	319.70(β)	0.964	0.4760	342.51(β)	1.000	0.5860	364.02(β)	1.033
0.3065	299.62(β)	0.930	0.3905	323.21(β)	0.974	0.4873	344.96(β)	1.005	0.6039	367.36(α)	1.038
0.3153	302.48(β)	0.937	0.4014	325.68(β)	0.976	0.5026	347.98(β)	1.008	1.0000	419.00(α)	1.000
0.3251	305.35(β)	0.942	0.4119	328.21(β)	0.980	0.5164	350.40(β)	1.008			
0.3355	308.15(β)	0.945	0.4230	330.95(β)	0.985	0.5308	352.93(β)	1.009			
					2-Methylpropan-2-ol						
0.0000	297.16(β)		0.2565	279.42(β)	0.858	0.3554	310.36(β)	0.917	0.4634	339.02(β)	0.987
0.0480	290.10(β)		0.2630	282.26(β)	0.868	0.3643	313.99(β)	0.935	0.4779	342.24(β)	0.993
0.0724	286.23(β)		0.2725	285.96(β)	0.879	0.3751	317.18(β)	0.943	0.4921	345.50(β)	1.000
0.0968	283.52(β)		0.2854	289.88(β)	0.883	0.3879	320.44(β)	0.949	0.5030	347.74(β)	1.000
0.1345	280.24(β)		0.2970	294.07(β)	0.895	0.4007	323.24(β)	0.950	0.5165	350.42(β)	1.000
0.1674	276.82(β)		0.3104	297.37(β)	0.893	0.4120	326.14(β)	0.956	0.5246	352.90(β)	1.000
0.1954	273.14(β)		0.3200	300.45(β)	0.900	0.4238	329.57(β)	0.967	1.0000	419.00(α)	1.000
0.2206	272.12(β)	0.905	0.3308	303.72(β)	0.907	0.4368	332.33(β)	0.969			
0.2382	278.27(β)	0.910	0.3422	306.62(β)	0.909	0.4487	335.24(β)	0.976			
					Hexan-1-ol						
0.2611	278.77(β)	0.835	0.3668	312.75(β)	0.914	0.5085	344.62(β)	0.959	0.7369	383.84(α)	0.992
0.2731	283.57(β)	0.850	0.3783	316.08(β)	0.923	0.5280	348.49(β)	0.965	0.7779	392.05(α)	1.012
0.2842	287.60(β)	0.861	0.3902	319.06(β)	0.928	0.5492	353.39(β)	0.980	0.8150	396.54(α)	1.006
0.2974	292.87(β)	0.880	0.4019	321.35(β)	0.926	0.5722	357.16(β)	0.981	0.8515	402.23(α)	1.013
0.3065	295.45(β)	0.883	0.4141	324.52(β)	0.933	0.5977	356.35(β)	0.931	0.8904	408.61(α)	1.025
0.3182	300.07(β)	0.901	0.4270	327.69(β)	0.939	0.6033	360.92(β)	0.969	0.9232	411.53(α)	1.015
0.3307	303.26(β)	0.902	0.4419	331.59(β)	0.950	0.6128	361.74(β)	0.963	0.9629	414.89(α)	1.002
0.3390	305.26(β)	0.902	0.4575	334.64(β)	0.951	0.6457	368.56(α)	0.982	1.0000	419.00(α)	1.000
0.3475	308.93(β)	0.921	0.4735	337.99(β)	0.955	0.6523	369.08(α)	0.977			
0.3565	310.78(β)	0.918	0.4908	341.27(β)	0.956	0.6922	371.71(α)	0.944			
					Dodecan-1-ol						
0.0000	297.50(β)		0.2997	306.62(β)	1.038	0.4391	341.19(β)	1.068	0.6452	379.66(α)	1.090
0.0388	296.71(β)		0.3106	309.78(β)	1.041	0.4601	345.68(β)	1.073	0.6768	383.81(α)	1.079
0.0505	296.33(β)		0.3236	312.97(β)	1.039	0.4680	347.20(β)	1.073	0.7135	389.17(α)	1.075
0.1076	295.63(β)		0.3337	316.45(β)	1.051	0.4805	349.94(β)	1.078	0.7742	396.78(α)	1.061
0.1381	294.98(β)		0.3469	319.64(β)	1.051	0.4924	352.54(β)	1.083	0.8184	400.52(α)	1.038
0.1630	294.48(β)		0.3569	322.24(β)	1.053	0.5101	355.36(β)	1.079	0.8526	404.74(α)	1.035
0.2074	293.73(β)		0.3684	325.07(β)	1.055	0.5185	356.76(β)	1.078	0.8830	406.96(α)	1.019
0.2250	293.40(β)		0.3778	327.35(β)	1.057	0.5298	358.78(β)	1.078	0.9127	409.88(α)	1.012
0.2375	292.92(β)		0.3869	329.71(β)	1.061	0.5459	361.34(β)	1.079	0.9406	413.57(α)	1.014
0.2571	292.35(β)	1.012	0.3995	332.88(β)	1.067	0.5550	363.23(β)	1.081	0.9685	415.64(α)	1.003
0.2682	295.39(β)	1.008	0.4130	336.08(β)	1.071	0.5741	365.96(β)	1.077	0.9954	418.88(α)	1.003
0.2778	298.62(β)	1.014	0.4200	337.91(β)	1.075	0.5979	371.46(α)	1.090	1.0000	419.00(α)	1.000
0.2880	302.50(β)	1.026	0.4302	339.66(β)	1.071	0.6188	374.77(α)	1.086			

Table 4. Experimental Solid−Liquid Equilibrium Temperatures (T) for 1,2-Dimethylmidazole (1) + Alcohol (2) Systems and γ_1 Experimental Activity Coefficients of Solute

x_1	T/K	γ_1	x_1	T/K	γ_1	x_1	T/K	γ_1	x_1	T/K	γ_1
					Ethanol						
0.5970	273.74	1.105	0.6692	283.80	1.112	0.7731	295.56	1.099	0.9162	306.60	1.039
0.6210	277.47	1.112	0.6981	287.35	1.110	0.8024	298.21	1.100	0.9505	309.10	1.028
0.6322	279.35	1.117	0.7281	291.27	1.112	0.8393	301.30	1.075	0.9753	311.27	1.023
0.6508	281.95	1.119	0.7502	293.45	1.105	0.8806	304.65	1.060	1.0000	311.50	1.000
					Propan-1-ol						
0.6251	273.20	1.048	0.7377	289.79	1.080	0.8497	299.91	1.046	0.9332	306.10	1.015
0.6461	276.87	1.061	0.7625	292.44	1.076	0.8639	301.05	1.041	0.9501	307.48	1.011
0.6652	279.52	1.064	0.7980	295.62	1.064	0.8790	301.78	1.031	0.9647	308.60	1.007
0.6767	281.86	1.075	0.8078	296.30	1.059	0.8904	302.92	1.030	0.9812	309.82	1.002
0.6962	284.47	1.077	0.8215	297.78	1.058	0.9044	303.88	1.024	1.0000	311.50	1.000
0.7160	286.88	1.077	0.8345	298.94	1.054	0.9182	305.13	1.022			
					Propan-2-ol						
0.5921	277.05	1.160	0.7247	289.53	1.096	0.8488	299.50	1.043	0.9735	309.05	1.003
0.6110	279.31	1.155	0.7526	291.46	1.078	0.8751	301.38	1.031	0.9889	310.28	1.000
0.6582	283.18	1.122	0.7791	293.76	1.068	0.9079	303.63	1.018	1.0000	311.50	1.000
0.6788	285.02	1.112	0.8059	296.44	1.063	0.9408	306.20	1.008			
0.7008	286.96	1.101	0.8336	298.58	1.051	0.9549	307.75	1.009			
					Butan-1-ol						
0.5704	267.50	1.070	0.6652	282.39	1.100	0.8030	296.13	1.063	0.9697	308.92	1.005
0.5812	269.20	1.072	0.6837	284.96	1.103	0.8318	298.35	1.051	0.9845	310.05	1.001
0.5907	272.50	1.099	0.7069	287.42	1.107	0.8604	300.94	1.044	1.0000	311.50	1.000
0.6066	274.84	1.102	0.7300	289.95	1.093	0.8872	302.86	1.033			
0.6288	277.20	1.094	0.7524	291.86	1.083	0.9181	304.78	1.018			
0.6465	279.66	1.096	0.7748	293.94	1.076	0.9529	307.53	1.009			
					Butan-2-ol						
0.6091	269.95	1.033	0.7087	284.35	1.057	0.8249	295.51	1.028	0.9610	308.02	1.005
0.6215	272.02	1.039	0.7211	285.79	1.056	0.8439	297.24	1.024	0.9739	308.95	1.001
0.6302	274.06	1.051	0.7357	287.18	1.051	0.8627	298.91	1.019	0.9842	309.92	1.000
0.6469	276.19	1.051	0.7489	288.62	1.050	0.8817	300.73	1.017	0.9973	311.30	1.000
0.6597	278.13	1.055	0.7636	289.98	1.045	0.9028	302.10	1.007	1.0000	311.50	1.000
0.6709	279.86	1.059	0.7787	291.59	1.044	0.9225	304.58	1.011			
0.6815	281.59	1.064	0.7928	292.54	1.036	0.9345	305.60	1.009			
0.6941	282.95	1.061	0.8084	294.44	1.037	0.9484	306.81	1.006			
					2-Methylpropan-2-ol						
0.0000	297.16		0.1102	282.15		0.5942	275.64	1.136	0.7973	296.20	1.072
0.0233	293.53		0.1169	281.58		0.6091	277.69	1.137	0.8185	297.67	1.060
0.0327	292.75		0.1247	280.50		0.6238	279.45	1.133	0.8435	299.33	1.047
0.0551	289.13		0.1471	277.68		0.6402	281.46	1.131	0.8689	301.12	1.036
0.0607	288.19		0.1485	277.52		0.6576	283.36	1.126	0.8956	303.06	1.025
0.0673	287.51		0.3819	256.73[a]		0.6749	285.50	1.124	0.9392	306.46	1.012
0.0742	286.47		0.5152	258.07	1.044	0.6920	286.94	1.115	0.9556	307.64	1.007
0.0772	286.45		0.5321	260.00	1.058	0.7117	288.76	1.106	0.9711	308.95	1.004
0.0822	285.40		0.5502	268.10	1.117	0.7330	291.01	1.102	0.9853	310.05	1.000
0.0913	284.40		0.5650	271.50	1.135	0.7556	292.76	1.089	1.0000	311.50	1.000
0.1023	283.46		0.5811	273.66	1.134	0.7769	294.26	1.077			
					Hexan-1-ol						
0.5207	268.12	1.180	0.6442	284.85	1.169	0.7920	297.90	1.099	0.9179	305.89	1.030
0.5312	270.95	1.199	0.6610	285.95	1.154	0.8158	299.43	1.084	0.9367	306.81	1.019
0.5520	274.10	1.200	0.6800	288.08	1.149	0.8365	300.73	1.072	0.9510	307.85	1.014
0.5706	275.92	1.187	0.6991	290.10	1.143	0.8522	301.83	1.064	0.9688	308.90	1.006
0.5900	278.79	1.189	0.7201	291.98	1.133	0.8687	302.84	1.055	0.9852	310.05	1.000
0.6098	280.70	1.176	0.7415	293.80	1.123	0.8842	303.60	1.045	1.0000	311.50	1.000
0.6280	282.23	1.163	0.7668	295.88	1.110	0.8999	304.65	1.037			
					Dodecan-1-ol						
0.0000	297.50		0.5948	281.61	1.219	0.7386	294.28	1.133	0.9157	305.60	1.029
0.0512	296.25		0.6037	282.33	1.212	0.7511	295.09	1.124	0.9253	306.12	1.023
0.1108	295.65		0.6131	283.24	1.206	0.7612	295.86	1.118	0.9363	306.90	1.020
0.1834	293.40		0.6274	284.59	1.197	0.7743	296.69	1.109	0.9461	307.20	1.019
0.2137	291.78		0.6371	285.66	1.193	0.7858	297.40	1.101	0.9576	308.01	1.016
0.2515	290.20		0.6472	286.58	1.187	0.7975	298.09	1.093	0.9704	308.50	1.010
0.3013	288.28		0.6565	287.50	1.182	0.8100	298.92	1.086	0.9770	309.31	1.007
0.3580	285.56		0.6665	288.50	1.178	0.8226	300.01	1.082	0.9818	309.62	1.000
0.4008	283.25		0.6760	289.42	1.173	0.8357	300.87	1.074	0.9882	310.50	1.000
0.4421	280.25		0.6853	290.20	1.168	0.8480	301.20	1.062	0.9939	311.02	1.000
0.5574	276.99	1.231	0.6963	290.96	1.159	0.8610	302.80	1.064	1.0000	311.50	1.000
0.5706	278.63	1.227	0.7067	291.82	1.153	0.8725	303.02	1.052			
0.5787	279.90	1.228	0.7175	292.96	1.150	0.8864	303.75	1.047			
0.5871	280.67	1.222	0.7276	293.27	1.138	0.9008	304.20	1.036			

[a] DSC measurement.

Table 5. Eutectic Temperatures, $T_{1,e}$, and Composition, $x_{1,e}$, Detected Graphically or by DSC for {Imidazole (1) + 2-Methylpropan-2-ol or Dodecan-1-ol (2)} Systems

system	$x_{1,e}$	T_e/K
1*H*-imidazole + 2-methylpropan-2-ol	0.26 ± 0.01	263.05 ± 0.1
2-methyl-1*H*-imidazole + 2-methylpropan-2-ol	0.22 ± 0.01	272.12 ± 0.1
1,2-dimethylimidazole + 2-methylpropan-2-ol	0.45 ± 0.02[a]	244.65 ± 0.1[a]
1*H*-imidazole + dodecan-1-ol	0.32 ± 0.02	291.45 ± 0.1
2-methyl-1*H*-imidazole + dodecan-1-ol	0.26 ± 0.02	292.35 ± 0.1
1,2-dimethylimidazole + dodecan-1-ol	0.56 ± 0.02	276.15 ± 0.1

[a] DSC measurement.

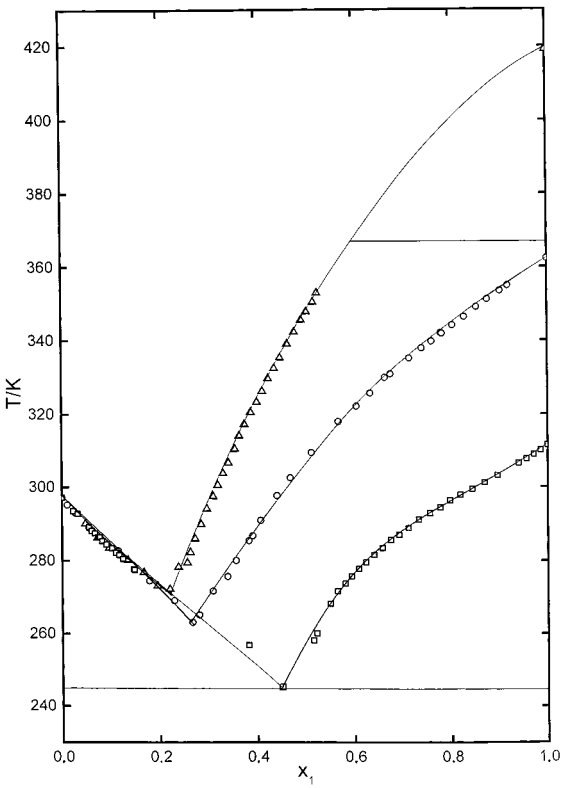

Figure 2. Solid−liquid equilibrium diagrams: ○, 1*H*-imidazole, or △, 2-methyl-1*H*-imidazole, or □, 1,2-dimethylimidazole (1) + 2-methylpropan-2-ol mixtures. Solid lines are from calculations by the Wilson equation.

Ubichem Limited Angleterre, >99%), 2-methylpropan-2-ol (3972-25-6, Aldrich, 99.5+%), hexan-1-ol (111-27-3 Reachim, 99%), dodecan-1-ol (112-53-8, Fluka AG, >99%), 1*H*-imidazole (288-32-4, Koch-Light Laboratory, 99%), 2-methyl-1*H*-imidazole (693-98-1, Koch-Light Laboratory, 99%), 1,2-dimethylimidazole (1739-84-0, Koch Light Laboratory, 98%). All solvents were fractionally distilled over different drying reagents to a mass fraction purity better than 0.998 and 0.999. 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 of its high hygroscopic tendency. All compounds were checked by GLC analysis, and no significant impurities were found. Analysis, using the Karl Fischer technique, showed that the impurity in each of the solvents was <0.02 mol %. Physical properties of pure imidazoles are collected in Table 1. Molar enthalpies of fusion have been measured by the differential scanning microcalorimeter Perkin-Elmer Pyris 1. Measurements of the fusion enthalpy were carried out at a scan rate of 2 K·min^{-1}, a power sensitivity of 16 mJ·s^{-1}, and a recorder sensitivity of 5 mV. The instrument was calibrated against a 99.9999 mol % purity indium sample. The calorimetric accuracy was ±1%, and the calorimetric precision was ±0.5%. The results are presented in Table 1. For 1*H*-imidazole the measured value of the enthalpy of fusion is much lower than the literature value (12.82 kJ·mol^{-1}).[6] It is difficult to explain such a difference when the temperature of melting is close to the literature one.[6] The molar heat capacities during the melting process, ΔC_{pm}, 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 the Microcalorimeter TG-DSC 111 for the higher temperatures for the ΔC_{pm} measurements (see Figure 1). The calorimetric accuracy was ±5 J·K^{-1}·mol^{-1}. The results for 1,2-dimethylimidazole deviate from the smoothed curve more than for other imidazoles because of the high higroscopy of that substance. However, these measured data are sufficiently reliable to provide a baseline for heat capacity changes during the melting point calculations.

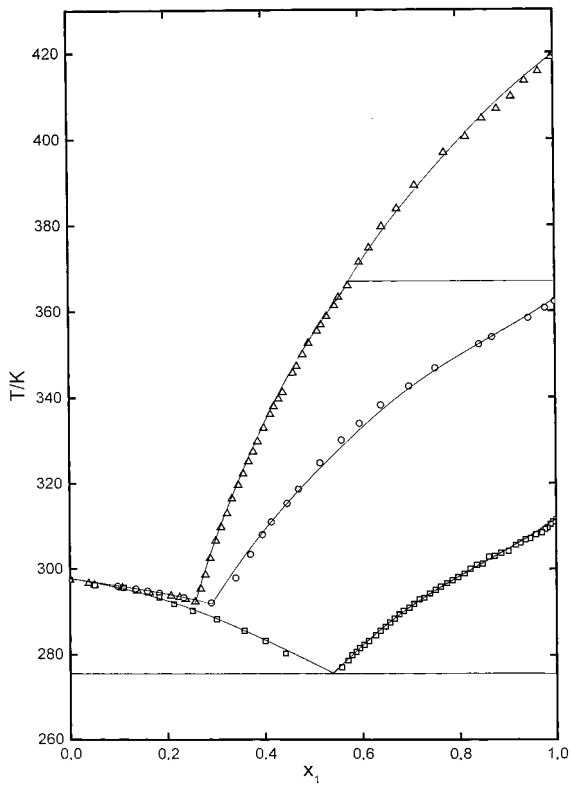

Figure 3. Solid−liquid equilibrium diagrams: ○, 1*H*-imidazole, or △, 2-methyl-1*H*-imidazole, or □, 1,2-dimethylimidazole (1) + dodecan-1-ol mixtures. Solid lines are from calculations by the Wilson equation.

Solid−liquid equilibrium (SLE) temperatures were determined using a dynamic method described in detail previously.[7] Mixtures were heated very slowly (at <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 Anschutz (TGL 11986, H. Schlegel, Ilmenau, Germany) thermometer (subdivided in 0.1 K) 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 ±0.05 K. Mixtures were prepared by weighing the pure components to within 2×10^{-4} g. Reproducibility of the measurements was 0.1 K, which corresponded to a relative error in composition of <1%.

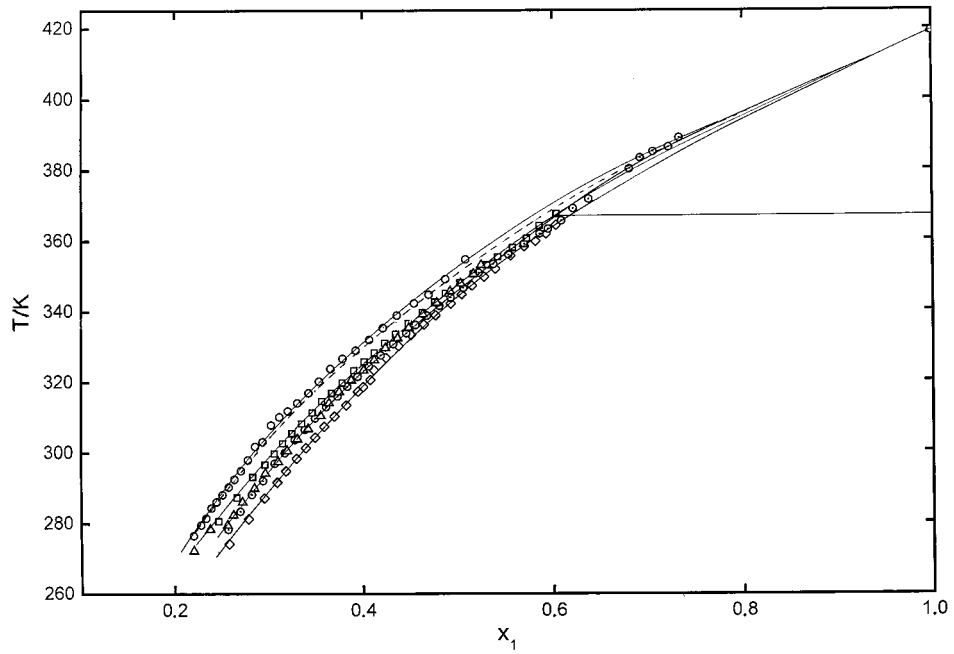

Figure 4. Solubility of 2-methyl-1*H*-imidazole in (◇) propan-1-ol, (○) propan-2-ol, (⊙) butan-1-ol, (□) butan-2-ol, and (△) 2-methylpropan-2-ol. Solid lines are from calculations by the NRTL 1 equation; dotted line designates ideal solubility.

Results and Discussion

Tables 2−4 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 saturated solution for the investigated systems. The experimental values of the eutectic temperature (T_e) and eutectic composition, $x_{1,e}$ (most of them determined graphically), observed in {imidazole + 2-methylpropan-2-ol or dodecan-1-ol} mixtures are collected in Table 5. The SLE diagrams of {imidazole (1) + 2-methylpropan-2-ol or dodecan-1-ol (2)} are presented in Figures 2 and 3, respectively.

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

(i) Positive deviations from ideality were found for most of the mixtures. Thus, the solubility is lower than the ideal one; $\gamma_1 > 1$, for all alcohols + 1*H*-imidazole or 1,2-dimethylimidazole systems (see the values of activity coefficients in Tables 2−4).

(ii) The solubility of 1*H*-imidazole and 2-methyl-1*H*-imidazole in alcohols decreases with increasing molecular weight of the alcohol.

(iii) The liquidus curves of the primary, secondary, and tertiary alcohols exhibit similar shapes; the differences in solubilities are small, and for 1*H*-imidazole and 2-methyl-1*H*-imidazole the solubility increases in order propan-1-ol > propan-2-ol, butan-1-ol > 2-methylpropan-2-ol > butan-2-ol (see Figure 4).

(iv) It was observed that the solubility of 1,2-dimethylimidazole in ethanol is smaller than in other alcohols (C_3 and C_4), and the order in primary, secondary, and tertiary alcohols is different from that for the other two imidazoles.

When the hydrogen atom connected with nitrogen is changed for a methyl group (1,2-dimethylimidazole + alcohol mixture), it is possible to observe only partly breakdown of the alcohol−alcohol association (see solubility in ethanol) and weaker alcohol−imidazole interaction. This is evidence that the interaction of hydrogen atom of 1*H*-imidazoles with the OH group of alcohols (1*H*-imidazole or 2-methyl-1*H*-imidazole + alcohol mixtures) is stronger than for the 1,2-dimethylimidazole + alcohol mixture. For 1,2-dimethylimidazole the solubility decreases in the order butan-2-ol > propan-1-ol > propan-2-ol > butan-1-ol > 2-methylpropan-2-ol > ethanol > hexan-1-ol > dodecan-1-ol. For 1*H*-imidazole and 2-methyl-1*H*-imidazole the solubility in 2-methylpropan-2-ol is higher than in butan-2-ol. This can be explained by considering the structural implications of the branched alcohol to A−B interaction. The inductive effect of the substituted methyl group on the side of the ring should result in an enhancement of A−B interaction. However, it is difficult to discuss because the melting temperature of 2-methyl-1*H*-imidazole is much higher than for the 1*H*-imidazole (see Table 1) and the solubilities generally decrease. The only evidence is that for 2-methyl-1*H*-imidazole the solubility is very close to the ideal and at lower temperatures is even higher than ideal solubility ($\gamma_1 < 1$).

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

$$-\ln x_1 = \frac{\Delta H_{m1}}{R}\left(\frac{1}{T} - \frac{1}{T_{m1}}\right) - \frac{\Delta C_{pm1}}{R}\left(\ln \frac{T}{T_{m1}} + \frac{T_{m1}}{T} - 1\right) + \ln \gamma_1 \quad (1)$$

where x_1, γ_1, ΔH_{m1}, ΔC_{pm1}, 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 point, melting point of the solute (1), and equilibrium temperature, respectively.

If a solid−solid transition occurs before fusion, an additional term must be added to the right-hand side of eq 1.[8,9] 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

$$-\ln x_1 = \frac{\Delta H_{m1}}{R}\left(\frac{1}{T} - \frac{1}{T_{m1}}\right) + \frac{\Delta H_{tr1}}{R}\left(\frac{1}{T} - \frac{1}{T_{tr1}}\right) - \frac{\Delta C_{pm1}}{R}\left(\ln \frac{T}{T_{m1}} + \frac{T_{m1}}{T} - 1\right) + \ln \gamma_1 \quad (2)$$

Table 6. Molar Volumes, V_m, and Association Parameters for Alcohols

alcohol	V_m(298.15 K) / cm^3·mol^{-1} [a]	$-\Delta H$ / kJ·mol^{-1} [b]	K (298.15 K)[b]
ethanol	58.7	22.96	89.8
propan-1-ol	72.7	22.76	70.5
propan-2-ol	77.0	22.58	44.4
butan-1-ol	92.0	22.53	54.6
butan-2-ol	92.4	22.18	30.3
2-methylpropan-2-ol	94.9	21.59	19.5
hexan-1-ol	125.3	22.15	35.4
dodecan-1-ol	224.7	21.10[c]	15.0[c]

[a] From ref 16. [b] From ref 17. [c] From linear extrapolation from other *n*-alcohols.

where ΔH_{tr1}, and T_{tr1} stand for enthalpy of transition and transition temperature of the solute, respectively. The existence of a solid−solid phase transition was observed only for 2-methyl-1*H*-imidazole by the DSC measurements and by a change of color from white crystals to yellow-brown crystals during the solubility measurements.

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 free energy of mixing, (G^E), the Wilson,[10] UNIQUAC ASM,[11] and NRTL 1[12] methods. The exact mathematical forms of the equations have been presented in our previous paper.[13]

Table 7. Correlation of the Solubility Data, SLE, of Imidazole (1) + 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[b]	UNIQUAC ASM σ[b]	NRTL σ[b]
alcohol	J mol^{-1}	J mol^{-1}	J mol^{-1}			
			1*H*-Imidazole			
ethanol	3179.25 4165.19	2298.52 −3024.73	4243.83 −6891.81	0.44	2.44	1.69
propan-1-ol	2855.92 4069.63	2046.37 −2712.00	3665.55 −5896.39	0.40	1.82	1.36
propan-2-ol	2248.06 3863.68	1719.37 −2313.90	3007.04 −4964.94	0.45	0.82	0.47
butan-1-ol	2057.81 3909.82	1670.35 −2189.29	2883.68 −4447.11	0.47	1.11	0.95
butan-2-ol	2056.95 4112.65	474.34 −1449.22	2763.14 −4337.30	0.64	0.63	0.84
2-methylpropan-2-ol	2154.15 4193.80	−609.85 −616.26	−1445.07 −1493.85	0.36	0.32	0.31
hexan-1-ol	1411.66 3368.70	1372.98 −1755.40	2138.48 −3112.99	0.45	0.62	0.69
dodecan-1-ol	640.89 4524.83	1547.77 −959.95	3714.78 −636.84	0.28	0.23	0.24
			2-Methyl-1*H*-imidazole			
ethanol	54170.5 −1231.7	1700.32 −2935.61	2254.75 −6309.48	2.47	2.75	1.57
propan-1-ol	66727.1 −2035.3	1023.90 −2481.54	849.91 −4933.88	1.78	1.66	1.46
propan-2-ol	−2739.33 4257.02	188.19 −1587.90	−181.16 −3247.21	0.78	0.84	0.84
butan-1-ol	67037.5 −2329.2	144.73 −1583.08	−232.90 −3289.93	2.51	1.72	1.71
butan-2-ol	63331.3 −2175.2	−462.25 −964.49	−1207.79 −2181.02	1.76	1.21	1.23
2-methylpropan-2-ol	59529.4 −2353.9	−496.91 −863.46	−1255.94 −1998.83	2.29	2.59	2.61
hexan-1-ol	1874.70 −2075.94	406.86 −1406.21	227.69 −2740.15	1.45	1.41	1.41
dodecan-1-ol	−614.05 5914.78	−2097.80 3392.35	−5385.26 3586.06	0.70	2.72	1.17
			1,2-Dimethylimidazole			
ethanol	−3917.18 9097.53	1318.42 −2435.49	1242.33 −5384.92	0.67	0.72	0.71
propan-1-ol	−3526.79 7332.95	−2296.35 2671.31	4921.94 −6541.82	0.33	0.56	0.49
propan-2-ol	−2282.53 4991.08	1959.77 −2240.00	4073.18 −5569.07	0.37	0.73	1.06
butan-1-ol	−2755.11 6565.12	1998.20 −2296.73	4179.12 −5289.43	0.56	1.25	0.69
butan-2-ol	−2699.86 5179.10	1981.64 −2299.88	3929.58 −5293.21	0.45	0.69	0.64
2-methylpropan-2-ol	−2600.51 6733.67	−3470.37 1628.62	−5505.49 708.97	1.29	0.78	0.79
hexan-1-ol	−1585.77 5899.65	1460.58 −1596.78	2912.69 −3364.01	0.32	0.33	0.33
dodecan-1-ol	87.31 4134.99	246.06 −272.48	203.16 −228.68	0.20	0.26	0.26

[a] Calculated with the third nonrandomness parameter $\alpha = 0.3$. [b] According to eq 4 in the text.

The parameters of the equations were found by an optimization technique using Marquardt's maximum neighborhood method of minimization[14]

$$\Omega = \sum_{i=1}^{n}[(\ln \gamma_i x_i)^{\text{exptl}} - (\ln \gamma_i x_i(P_1,P_2))^{\text{calcd}}]^2 \qquad (3)$$

where Ω is the objective function, $(\ln \gamma_1 x_1)^{\text{exptl}}$ denotes the experimental logarithm of activities of the ith point for a given concentration x_{1i}, and $(\ln \gamma_1 x_1)^{\text{calcd}}$ is the calculated logarithm of activities for a given concentration x_{1i} and parameters P_1 and P_2, obtained by solving the nonlinear equation (eq 1 or eqs 1 and 2), depending upon the value of temperature and the expression for the logarithm of the activity according to the assumed model. The nonlinear equations were solved using the secant method. The root-mean-square deviation of temperature (σ defined by eq 4) was used as a measure of the goodness of the solubility correlation.

$$\sigma = \left(\sum_{i=1}^{n}\frac{((\ln \gamma_i x_i)^{\text{exptl}} - (\ln \gamma_i x_i)^{\text{calcd}})^2}{n-2}\right) \qquad (4)$$

where $(\ln \gamma_1 x_1)^{\text{exptl}}$ and $(\ln \gamma_1 x_1)^{\text{calcd}}$ are, respectively, the experimental and calculated logarithms of activities of the ith point, 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 ASM and NRTL 1 equations were obtained by means of the following simple relationships:[15]

$$r_i = 0.029281V_m \qquad (5)$$

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

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 $l_i = 0$. Calculations with the UNIQUAC ASM and NRTL 1 models were carried out by use of the data set of association for alcohols presented in Table 6. The temperature dependence of association constants was calculated from the van't Hoff relationship assuming the enthalpy of hydrogen-bond formation to be temperature independent. The Mecke−Kempter model of association for developing two adjustable parameters was used. It was shown[18] that a proper value of α_{12} can be specified a priori, its value depending on the binary system and varying from 0.2 to 0.47. If α_{12} is assigned, the modified NRTL 1 equation has two adjustable parameters per binary: Δu_{12} and Δu_{21}. In this work, for imidazole + alcohol mixtures, parameter α_{12}, a constant of proportionality similar to the nonrandomness constant of the NRTL 1 equation ($\alpha_{12} = \alpha_{12} = 0.3$), was taken into account in calculations.

Table 7 lists the results of fitting the solubility curves by the three equations used: Wilson, UNIQUAC ASM, and NRTL 1.

For the 24 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 $\sigma = 0.89$. The results of correlations of imidazole in aliphatic alcohols (C_3−C_{12}) with respect to the occurrence of the alcohol association present slightly worse deviations of $\sigma = 0.98$ and $\sigma = 1.17$ for NRTL 1 and UNIQUAC ASM, respectively. This is evidence that also the solute−solvent interaction influences the behavior of the mixtures. It can be noted, however, that for 2-methyl-1*H*-imidazole the description is much worse and the average standard mean deviations are $\sigma = 1.72$, $\sigma = 1.86$, and $\sigma = 1.50$ for the Wilson, UNIQUAC ASM, and NRTL 1 equations, respectively.

If the solubilities in alcohols are very similar, which was observed for 1*H*-imidazole, the values of parameters for the certain model are also very close to each other (see Table 7).

Conclusions

The phenomenon of the solid−solid phase transition for 2-methyl-1*H*-imidazole has been observed. The solubility of 1*H*-imidazole and 2-methyl-1*H*-imidazole in alcohols decreases with increasing molecular weight of the alcohol. 1,2-Dimethylimidazole does not exhibit intramolecular A−A hydrogen bonding and has a low melting temperature and a low enthalpy of fusion. The solubility of 1,2-dimethylimidazole in alcohols shows an order different from that of the two other imidazoles; weaker alcohol−1,2-dimethylimidazole interaction is also observed.

The best results for the correlation of experimental points in binary systems of imidazoles in alcohols were obtained by means of the two-parameter Wilson equation with the root-mean-square deviation $\sigma = 0.89$. For better description a model covering A−A and A−B association is needed.

Acknowledgment

We gratefully acknowledge Prof. A. Książczak and Prof. H. Piekarski for some DSC measurements and Grysam Alexandre for technical assistance with some solubility measurements.

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Received for review April 20, 2001. Accepted August 23, 2001.

JE0101303