

# Solubility of 1-Dodecyl-3-methylimidazolium Chloride in Alcohols (C<sub>2</sub>–C<sub>12</sub>)<sup>†</sup>

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The solubility of 1-dodecyl-3-methylimidazolium chloride [C<sub>12</sub>mim][Cl] in alcohols {ethanol, 1-butanol, 1-hexanol, 1-octanol, 1-decanol, 1-dodecanol, 2-butanol, 2-methyl-2-propanol (*tert*-butyl alcohol)} has been measured by a dynamic method from 270 K to the melting point of the ionic liquid or to the boiling point of the solvent. The melting point, enthalpy of fusion, and enthalpies of four solid–solid phase transitions were determined by differential scanning calorimetry. The solubility of [C<sub>12</sub>mim][Cl] in primary alcohols decreases with an increase of the molecular weight of the alcohol from C<sub>6</sub> to C<sub>12</sub>. The difference of solubilities in alcohols C<sub>2</sub>–C<sub>4</sub> exists only in  $\alpha_1$  and  $\gamma_1$  solid crystalline phases. The difference between the primary, the secondary, and the tertiary alcohols is not significant. The intermolecular solute–solvent interaction of the  $\alpha$  stable crystalline solid form is higher for tertiary and secondary alcohol. The data were correlated by means of the Wilson, UNIQUAC ASM, and modified NRTL equations utilizing parameters derived from the solid–liquid equilibrium. The root mean square deviations of the solubility temperatures for all calculated data are higher than 7 K and depend on the particular equation used. The high enthalpy of solid–solid ( $\alpha_1 \rightarrow \beta_1$ ) phase transition is the main reason that the correlation of the solubility curves is not satisfied.

## Introduction

The continuing search for the new generation of solvents for catalysis, synthesis, and thermal storage is constantly revealing new substances with both useful and environmentally benign properties in chemical processes.<sup>1</sup> The ionic liquids (ILs) are generally salts based on a substituted imidazolium cation and an inorganic anion such as halide, [AlCl<sub>4</sub>]<sup>−</sup>, [BF<sub>4</sub>]<sup>−</sup>, or [PF<sub>6</sub>]<sup>−</sup> and are often liquids at room temperature.<sup>2–4</sup> Room temperature ILs are one of the goals of green chemistry because they create a cleaner and more sustainable chemistry. They are an important topic that has received more and more attention in recent years.<sup>2–12</sup> ILs are receiving increasing interest as environmentally friendly solvents for a range of synthetic and catalytic processes.<sup>1,13–15</sup> Clean technology concerns the reduction of waste from an industrial chemical process to a minimum: it requires the rethinking and redesign of many current chemical processes. Using ILs as solvents is one of the main strategies of clean industrial technology.<sup>1</sup> A major reason for the interest in ILs is their negligible vapor pressure, which decreases the risk of technological exposure and the loss of solvent to the atmosphere.<sup>12,16</sup> Most ILs are hygroscopic, which has significant practical implications. The qualitative and quantitative vapor–liquid equilibrium and liquid–liquid phase behavior of water and three ILs, 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF<sub>6</sub>]), 1-*n*-octyl-3-methylimidazolium hexafluorophosphate ([C<sub>8</sub>mim][PF<sub>6</sub>]), and 1-*n*-octyl-3-methylimidazolium tetrafluoroborate ([C<sub>8</sub>mim][BF<sub>4</sub>]), have been reported.<sup>17,18</sup> The presence of water in the IL phase can dramatically affect the physical properties.<sup>19,20</sup> The problem of miscibility of ILs with the water can affect properties, as clearly demonstrated for the viscosity and density,<sup>21</sup> surface tension,<sup>21</sup> and polarity.<sup>22</sup> The synthesis method of ILs has been reported.<sup>4,23–27</sup> The synthesis methods of halide ILs are described elsewhere.<sup>28,29</sup>

The solubility of three imidazoles in alcohols was presented by us earlier.<sup>30</sup> It was noted that the solubility in alcohols is lower than in water. We have begun a systematic investigation into the thermodynamic properties and phase equilibria of simple imidazole molecules,<sup>30,31</sup> benzimidazoles,<sup>31</sup> and phenylimidazoles<sup>32</sup> as well as the new class of their ionic salts. The densities, surface tensions, octanol/water partition coefficients, and solid–liquid (SLE) and liquid–liquid (LLE) equilibria of many binary mixtures are under investigation. The purpose of this paper is to report the solubility of 1-dodecyl-3-methylimidazolium chloride [C<sub>12</sub>mim][Cl] in alcohols: ethanol, 1-butanol, 1-hexanol, 1-octanol, 1-decanol, 1-dodecanol, 2-butanol, and 2-methyl-2-propanol (*tert*-butyl alcohol).

## Experimental Procedures and Results

From differential scanning microcalorimetry (DSC) data, the melting point, enthalpies of fusion, temperatures of solid–solid phase transitions I ( $\alpha_1 \rightarrow \beta_1$ ), II ( $\beta_1 \rightarrow \gamma_1$ ), III, and IV, and enthalpies of solid–solid phase transitions have been measured. The (solid + liquid) phase diagrams for IL in alcohols (C<sub>2</sub>–C<sub>12</sub>) have been measured by a dynamic method from 270 K to the melting point of salt or to the boiling point of an alcohol.

**Materials.** The [C<sub>12</sub>mim][Cl] produced by solvent innovation GmbH, Köln, Germany, was used without any further purification. Its purity was  $\geq 98$  mass percent. This substance was packed under the nitrogen. Samples for the solubility measurements were provided also under the nitrogen in the dry box. All alcohols were produced by Sigma-Aldrich Chemie GmbH, Steinheim, Germany. The solvents were fractionally distilled over different drying reagents to a mass fraction purity better than 0.998 or 0.999. Liquids were stored over freshly activated molecular sieves of type 4A (Union Carbide). Analysis for the water contamination using the Karl Fischer technique for the alcohols showed that the impurity in each of the solvents was  $< 0.02$  mol %.

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**TABLE 1: Physical Constants of Pure [C<sub>12</sub>mim][Cl]: Melting Point,  $T_m$ ; Enthalpy of Fusion,  $\Delta H_m$ ; Temperatures of Solid–Solid Phase Transitions I–IV,  $T_{tr}$ ; and Enthalpies of Solid–Solid Phase Transitions,  $\Delta H_{tr}$ , as Determined from DSC Data**

salt	$T_m$ (K)	$\Delta H_m$ (kJ mol <sup>-1</sup> )	$T_{trI}/T_{trII}/T_{trIII}/T_{trIV}$ (K)	$\Delta H_{trI}/\Delta H_{trII}/\Delta H_{trIII}/\Delta H_{trIV}$ (kJ mol <sup>-1</sup> )
[C <sub>12</sub> mim][Cl]	369.78	0.604	310.15/283.21/270.61/235.34	23.580/1.157/1.457/0.158

**TABLE 2: Solubility Measurements of [C<sub>12</sub>mim][Cl] in Ethanol**

$x_1$	$T_{\gamma 1}$ (K)	$x_1$	$T_{\gamma 1}$ (K)
0.2511	273.78	0.4751	299.65
0.3018	284.08	0.5133	301.15
0.3585	291.82	0.5232	301.75
0.4253	296.40		
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$x_1$	$T_{\beta 1}$ (K)	$x_1$	$T_{\beta 1}$ (K)
0.5554	303.06	0.6347	316.05
0.5783	306.30	0.6417	316.09
0.5888	308.22	0.6516	316.27
0.6101	310.85	0.6980	316.81
0.6161	312.63	0.7196	317.36
0.6246	314.45		
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$x_1$	$T_{\alpha 1}$ (K)	$x_1$	$T_{\alpha 1}$ (K)
0.7293	318.18	0.8928	325.07
0.7564	319.65	0.9038	325.65
0.8076	321.93	0.9523	328.85
0.8281	323.85	1.0000	369.78

**TABLE 3: Solubility Measurements of [C<sub>12</sub>mim][Cl] in 1-Butanol**

$x_1$	$T_{\gamma 1}$ (K)	$x_1$	$T_{\gamma 1}$ (K)
0.2627	275.65	0.3712	288.34
0.2923	280.65	0.4164	292.16
0.3461	286.33	0.4450	294.72
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$x_1$	$T_{\beta 1}$ (K)	$x_1$	$T_{\beta 1}$ (K)
0.4682	298.88	0.5586	311.82
0.4838	303.58	0.5774	311.98
0.4978	307.23	0.6250	312.40
0.5447	311.78	0.6381	312.55
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$x_1$	$T_{\alpha 1}$ (K)	$x_1$	$T_{\alpha 1}$ (K)
0.7021	314.04	0.8337	333.19
0.7357	319.09	0.8601	337.92
0.7695	323.15	0.8818	340.33
0.7956	327.62	0.9206	348.63
0.8248	332.18	0.9417	351.13
0.8327	333.02	1.0000	369.78

**TABLE 4: Solubility Measurements of [C<sub>12</sub>mim][Cl] in 2-Butanol**

$x_1$	$T_{\beta 1}$ (K)	$x_1$	$T_{\beta 1}$ (K)
0.3815	277.70	0.5000	307.80
0.4032	286.58	0.5108	308.22
0.4216	292.36	0.5352	310.76
0.4303	294.12	0.5697	311.90
0.4417	297.54	0.6017	312.79
0.4568	301.42	0.6366	313.91
0.4627	302.46	0.6604	314.38
0.4725	303.36	0.7006	315.03
0.4795	305.28		
<hr/>			
$x_1$	$T_{\alpha 1}$ (K)	$x_1$	$T_{\alpha 1}$ (K)
0.7293	317.18	0.8740	328.86
0.7675	319.30	0.9250	345.20
0.8115	321.18	0.9812	362.66
0.8470	325.34	1.0000	369.78

**Procedures.** Molar enthalpies of fusion and solid–solid phase transitions have been measured by the differential scanning microcalorimeter Perkin-Elmer Pyris 1. Measurements of the fusion enthalpies were carried out at a scan rate of 2 K min<sup>-1</sup> or 10 K min<sup>-1</sup>, a power sensitivity of 16 mJ s<sup>-1</sup>, and a recorder

**TABLE 5: Solubility Measurements of [C<sub>12</sub>mim][Cl] in *tert*-Butyl Alcohol**

$x_1$	$T_{\alpha 2}$ (K)	$x_1$	$T_{\alpha 2}$ (K)
0.0000	297.99	0.0962	286.48
0.0040	296.96	0.1029	286.06
0.0081	296.42	0.1161	284.48
0.0106	296.08	0.1349	282.09
0.0334	294.73	0.1517	278.56
0.0662	290.95	0.1676	275.65
0.0896	287.02		
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$x_1$	$T_{\gamma 1}$ (K)	$x_1$	$T_{\gamma 1}$ (K)
0.1874	277.29	0.3977	295.36
0.2121	279.65	0.4313	298.35
0.2266	281.19	0.4413	299.04
0.2532	283.28	0.4703	302.66
0.2797	285.65	0.4937	304.25
0.3293	289.15	0.5050	305.48
0.3595	291.82	0.5128	305.59
0.3642	291.96	0.5218	306.54
0.3737	292.92	0.5350	307.55
0.3907	294.85		
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$x_1$	$T_{\beta 1}$ (K)	$x_1$	$T_{\beta 1}$ (K)
0.5536	308.69	0.6264	310.80
0.5766	308.95	0.6662	312.78
0.5776	309.03	0.6752	314.21
0.6126	309.93		
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$x_1$	$T_{\alpha 1}$ (K)	$x_1$	$T_{\alpha 1}$ (K)
0.6978	318.11	0.8356	324.85
0.7332	319.69	0.8464	325.13
0.7537	320.45	0.9024	328.72
0.7891	322.29	0.9452	332.89
0.8253	324.45		

sensitivity of 5 mV. The instrument was calibrated against a 99.9999 mol % purity indium sample. The calorimetric accuracy was  $\pm 1\%$ , and the calorimetric precision was  $\pm 0.5\%$ .

Solid solubilities have been determined using a dynamic (synthetic) method, described in detail previously.<sup>33</sup> Mixtures of solute and solvent were prepared by weighing the pure components to within  $1 \times 10^{-4}$  g. The sample of solute and alcohol was heated very slowly (at less than 2 K h<sup>-1</sup> 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 a calibrated GALENKAMP AUTOTHERM II thermometer totally immersed in the thermostating liquid. Measurements were carried out over a wide range of solute mole fraction from 0 to 1. The thermometer was calibrated on the basis of the ITS-90 scale of temperature. The accuracy of temperature measurements was  $\pm 0.01$  K while the error of mole fraction did not exceed  $\delta x_1 = 0.0005$ . The difference with our previous published results of solubilities<sup>30–33</sup> (and the literature cited in) is that every experimental point was obtained from a new sample. Additionally, it was found that the solution–crystallization procedure was quite slow and difficult, thus the solubility measurements were very time-consuming.

**Results.** Table 1 shows the pure component DSC results. A search of literature has indicated that data for [C<sub>12</sub>mim][Cl], presented here, have not been reported previously. The solubilities of [C<sub>12</sub>mim][Cl] in 1-alcohols are shown in Tables 2–9. The tables include the direct experimental results of the SLE

**TABLE 6: Solubility Measurements of [C<sub>12</sub>mim][Cl] in 1-Hexanol**

$x_1$	$T_{\gamma 1}$ (K)	$x_1$	$T_{\gamma 1}$ (K)
0.2007	273.24	0.4481	298.23
0.2229	280.99	0.4752	300.38
0.2528	285.78	0.5052	301.30
0.3056	289.02	0.5158	301.40
0.3730	291.88	0.5302	301.72
0.4115	293.62	0.5638	302.28
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$x_1$	$T_{\beta 1}$ (K)	$x_1$	$T_{\beta 1}$ (K)
0.5785	303.49	0.7170	321.11
0.5834	303.18	0.7352	321.89
0.6110	305.20	0.7514	323.56
0.6424	310.12	0.7595	323.69
0.6754	312.38	0.7800	324.07
0.6863	314.02	0.8039	324.13
0.6905	313.48	0.8133	324.16
0.7019	318.18	0.8264	324.35
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$x_1$	$T_{\alpha 1}$ (K)	$x_1$	$T_{\alpha 1}$ (K)
0.8460	325.57	0.9354	333.89
0.8927	330.36	0.9511	336.74
0.9247	333.15	1.0000	369.78

**TABLE 7: Solubility Measurements of [C<sub>12</sub>mim][Cl] in 1-Octanol**

$x_1$	$T_{\gamma 1}$ (K)	$x_1$	$T_{\gamma 1}$ (K)
0.1864	272.72	0.3666	294.25
0.1947	274.25	0.3725	294.72
0.2154	277.52	0.3773	294.70
0.2350	280.27	0.3949	295.37
0.2551	282.85	0.4166	296.03
0.2888	287.76	0.4369	296.46
0.3004	289.62	0.4392	296.55
0.3340	292.10	0.4526	296.95
0.3502	292.98		
<hr/>			
$x_1$	$T_{\beta 1}$ (K)	$x_1$	$T_{\beta 1}$ (K)
0.4638	298.90	0.6406	315.32
0.4861	300.36	0.6600	315.95
0.5142	304.16	0.6773	316.66
0.5459	307.72	0.6978	316.62
0.5818	310.94	0.7154	316.72
0.5951	312.62	0.7308	317.26
0.6186	314.23		
<hr/>			
$x_1$	$T_{\alpha 1}$ (K)	$x_1$	$T_{\alpha 1}$ (K)
0.7508	318.91	0.8508	331.86
0.7647	320.19	0.9316	355.18
0.8000	323.54	1.0000	369.78
0.8264	329.67		

temperatures,  $T_1$  or  $T_2$  ( $\alpha_1$ ,  $\beta_1$ , or  $\gamma_1$  stable crystalline forms) vs  $x_1$ , the mole fraction of the [C<sub>12</sub>mim][Cl] in the saturated solution for the investigated systems. Table 10 shows the temperatures and compositions of the eutectic points for the investigated mixtures.

## Discussion

**DSC.** From the thermograph of pure solute, it can be noted that [C<sub>12</sub>mim][Cl] exhibits a mesomorphic plastic phase ( $\alpha_1$ ) in the region from 369.8 to 310.15 K with a very small heat of melting transition equal to 0.604 kJ mol<sup>-1</sup>. On the other hand, the transition of [C<sub>12</sub>mim][Cl] plastic phase  $\alpha_1$  into crystalline phase  $\beta_1$  is accompanied by the unbelievably high heat effect equal to 23.580 kJ mol<sup>-1</sup>. Between 283 and 200 K, the next three solid–solid phase transitions are observed with the enthalpies of phase transitions ( $\Delta H_{\text{trII}}$ ,  $\Delta H_{\text{trIII}}$ , and  $\Delta H_{\text{trIV}}$ ) less than 5% of the previous one. During the repeatable DSC experiment, no glass phase was observed for [C<sub>12</sub>mim][Cl] in

**TABLE 8: Solubility Measurements of [C<sub>12</sub>mim][Cl] in 1-Decanol**

$x_1$	$T_{\alpha 2}$ (K)	$x_1$	$T_{\alpha 2}$ (K)
0.0000	280.50	0.0204	279.59
0.0099	280.30	0.0339	278.90
<hr/>			
$x_1$	$T_{\gamma 1}$ (K)	$x_1$	$T_{\gamma 1}$ (K)
0.0449	280.32	0.2201	298.92
0.0591	281.16	0.2722	303.65
0.0734	282.75	0.2967	305.45
0.0819	283.52	0.2987	305.85
0.0927	284.65	0.3413	305.57
0.1036	286.68	0.3519	307.25
0.1131	287.52	0.3909	309.24
0.1246	288.67	0.3918	309.30
0.1442	289.88	0.3940	309.15
0.1682	292.24	0.4298	309.08
0.1854	294.95	0.4596	309.04
<hr/>			
$x_1$	$T_{\beta 1}$ (K)	$x_1$	$T_{\beta 1}$ (K)
0.4740	309.52	0.5912	316.44
0.4768	309.96	0.5997	316.66
0.5302	313.30	0.6383	318.11
0.5768	316.02		
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$x_1$	$T_{\alpha 1}$ (K)	$x_1$	$T_{\alpha 1}$ (K)
0.6855	320.03	0.9010	348.14
0.7216	324.49	0.9320	351.83
0.7613	329.61	0.9700	360.28
0.8235	335.29	1.0000	369.78
0.8680	342.62		

**TABLE 9: Solubility Measurements of [C<sub>12</sub>mim][Cl] in 1-Dodecanol**

$x_1$	$T_{\alpha 2}$ (K)	$x_1$	$T_{\alpha 2}$ (K)
0.0000	296.84	0.0134	295.59
0.0063	296.65		
<hr/>			
$x_1$	$T_{\gamma 1}$ (K)	$x_1$	$T_{\gamma 1}$ (K)
0.0205	296.68	0.0697	302.59
0.0246	297.14	0.0729	303.00
0.0269	297.35	0.0790	303.09
0.0327	297.54	0.0874	303.69
0.0360	297.69	0.1028	303.45
0.0365	297.72	0.1308	303.45
0.0399	297.73	0.1368	303.85
0.0420	298.56	0.1474	303.83
0.0449	298.66	0.1619	303.65
0.0459	298.72	0.1672	304.85
0.0541	299.32	0.1724	303.98
0.0593	301.02		
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$x_1$	$T_{\beta 1}$ (K)	$x_1$	$T_{\beta 1}$ (K)
0.1808	303.94	0.2981	309.93
0.2001	305.98	0.3262	310.28
0.2160	306.88	0.3499	310.18
0.2237	307.52	0.3761	310.23
0.2374	308.53	0.3898	310.11
0.2478	308.82	0.4214	310.66
0.2711	309.52		
<hr/>			
$x_1$	$T_{\alpha 1}$ (K)	$x_1$	$T_{\alpha 1}$ (K)
0.4592	311.34	0.6898	317.96
0.4899	312.39	0.7464	321.54
0.5248	313.27	0.8044	324.30
0.5401	313.63	0.8491	332.95
0.5755	314.65	0.9246	348.64
0.6067	315.82	1.0000	369.78
0.6388	316.94		

the temperature range from 200 to 400 K. The data reported in Table 1 are the average of the five experimental DSC diagrams made for the different samples. Our solubility measurements were provided up to about 273 K; thus, only two phase

**TABLE 10: Eutectic Temperatures,  $T_{1,e}$ , and Compositions,  $x_{1,e}$ , Detected Graphically for  $[C_{12}mim][Cl]$  + (*tert*-Butyl Alcohol or 1-Decanol or 1-Dodecanol)**

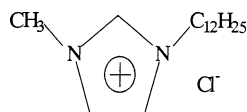
mixtures	$T_{1,e}$ (K)	$x_{1,e}$
$[C_{12}mim][Cl]$ + <i>tert</i> -butyl alcohol	270.30	0.1670
$[C_{12}mim][Cl]$ + 1-decanol	278.84	0.0358
$[C_{12}mim][Cl]$ + 1-dodecanol	295.67	0.0130

transitions were observed. The solid–solid phase transition temperatures,  $T_{trI}$  and  $T_{trII}$ , of  $[C_{12}mim][Cl]$  were confirmed by solubility measurements as two inflections on the liquidus curve but in much higher temperatures.

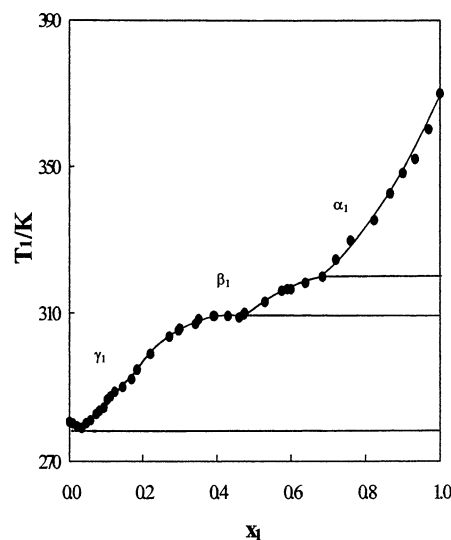
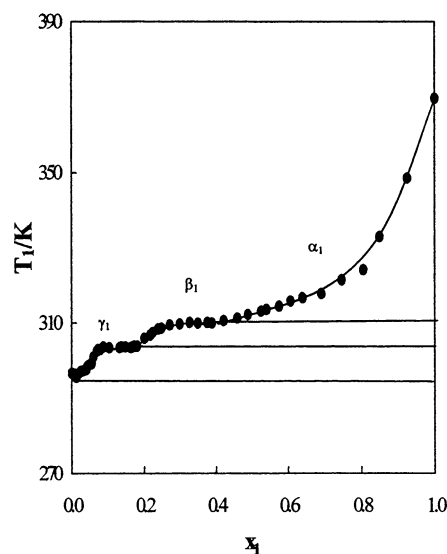
For simple imidazoles, only 2-methyl-1*H*-imidazole has shown a solid–solid phase transition with the enthalpy of the transition lower than that of fusion.<sup>30</sup> On the other hand, the *n*-alkanes  $C_{20}$ – $C_{44}$  undergo a solid–solid transition showing different crystalline forms.<sup>34,35</sup> The transitions are related to rotation of molecular chains about their long axes. The atomic structure of the low temperature crystalline phase of even-numbered paraffins has also been determined.<sup>36,37</sup> More recently, the main structural features of the high temperature rotator phases have been established as well.<sup>35</sup> In our solute, the dodecyl substituent in the position 1 of the molecule ring may cause a high degree of orientational disorder of the molecules of hydrogen-bonded net of IL.

Similar behavior to  $[C_{12}mim][Cl]$  was shown by sulfolane with the enthalpy of fusion ( $1.43 \text{ kJ mol}^{-1}$ ), which was four times lower than the enthalpy of the solid–solid phase transition ( $5.35 \text{ kJ mol}^{-1}$ ).<sup>38</sup> X-ray crystal analysis for some ILs was presented by many authors.<sup>24,25,28,29,39,40</sup> For the ILs molecules composed of a rigid and polarizable core attached to one or two aliphatic chains, they often give liquid–crystal mesophases when heated, especially salts having alkyl chain lengths of  $n > 12$ .<sup>28</sup> Also, the melting point phase diagrams for different ILs as a function of alkyl chain length  $n$  show that  $C_{12}$  is the border of melting transitions from crystalline form or clearing point of liquid crystalline form.<sup>1,41</sup> In particular, when the alkyl chains are long, smectic phases tend to result due to the microphase separation of the polarizable core and the aliphatic tail portions. The first long chain imidazolium salts, whose crystal structure has been reported, were  $[C_{12}mim][PF_6]$ <sup>24</sup> and 1,3-didodecylbenzimidazolium chloride  $[(C_{12})_2Bim][Cl]$ .<sup>29</sup> The chain configuration and the lack of any disorder in the structure appear to be a consequence of the interdigitated molecular packing. The twist in the alkyl chain occurs over a larger number of carbon atoms in ILs than observed in the  $[(C_{12})_2Bim][Cl]$  salt. The unit cell of the  $[C_{12}mim][PF_6]$  salt was described as having a spoon-shaped structure and different from that of  $[(C_{12})_2Bim][Cl]$ .<sup>24</sup> The crystal structure of ILs is very important and is responsible for the SLE and LLE in binary mixtures of ILs with different solvents.

**SLE.** The ability of a solute to form hydrogen bonds with potential solvents is an important feature of its behavior. Basic  $[C_{12}mim][Cl]$  IL can act as both a hydrogen bond acceptor ( $[Cl]^-$ ) and a donor ( $[C_{12}mim]^+$ ) and would be expected to interact with solvents have both accepting and donating sites.



On the other hand, alcohols are very well-known to form hydrogen-bonded solvents with both high enthalpies of association and association constants. Hence, they would be expected to stabilize solute with hydrogen bond donor sites.

**Figure 1.** SLE diagram for  $[C_{12}mim][Cl]$  in 1-decanol.**Figure 2.** SLE diagram for  $[C_{12}mim][Cl]$  in 1-dodecanol.

Experimental phase diagrams of SLE investigated in this work are characterized mainly by the following: (i) the solubility of  $[C_{12}mim][Cl]$  in alcohols decreases with an increase of the molecular weight of an alcohol from  $C_2$  to  $C_{12}$ ; (ii) the liquidus curves of the primary, secondary, and tertiary alcohols exhibit similar shapes; the differences in solubilities are small and are shown mainly in  $\alpha$  and  $\gamma$  solid phases; the solubility increases in the order *tert*-butyl alcohol  $>$  2-butanol  $>$  1-butanol and 2-butanol  $>$  1-butanol  $>$  *tert*-butyl alcohol for the high temperature  $\alpha$  and low temperature  $\gamma$  phase, respectively; (iii) the complete phase diagrams were found to be eutectic mixtures (see Figures 1–3); (iv) positive deviations from ideality were found, thus the solubility is lower than the ideal one; the activity coefficient of solute is higher than 1 ( $\gamma_1 > 1$ ) (see Figure 4); (v) the liquidus curves of  $[C_{12}mim][Cl]$  have shown two characteristic inflections of solid–solid phase transitions.

As it is shown in Figures 1–4 and Tables 2–9, the solid–solid phase transition for the mixture was not a sharp transition at the same temperature as observed for the pure salt but was spread over a range of several degrees in different solvents. It was observed previously for the mixtures of the ILs.<sup>24</sup> For the crystal solute, the solid–solid phase transition temperature  $T_{tr}$  is a property of the pure solid and is expected to be not affected by the solvent–solute interactions. However, it was



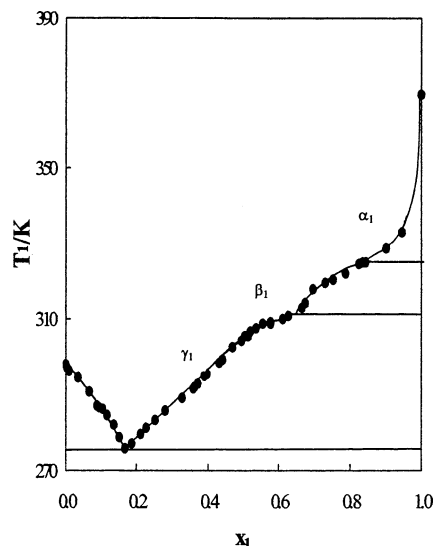


Figure 3. SLE diagram for [C<sub>12</sub>mim][Cl] in *tert*-butyl alcohol.

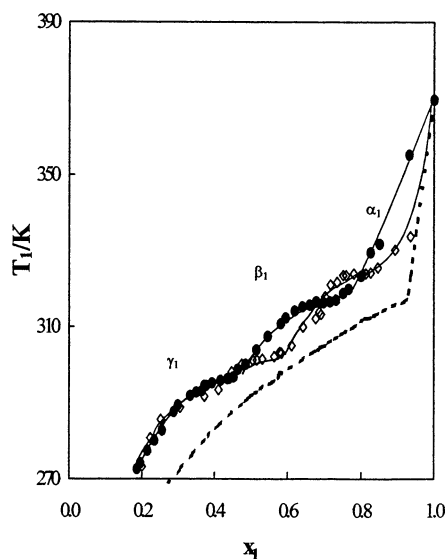


Figure 4. Solubility of [C<sub>12</sub>mim][Cl] in (◇) 1-hexanol and (●) 1-octanol; the dotted line is designated ideal solubility.

noted by us previously that for *n*-alkanes,<sup>42</sup> *n*-alkanols,<sup>43,44</sup> crown-ethers,<sup>45</sup> and cholesterol<sup>46</sup> the changes of phase transition temperatures in different solvents were observed. It has to be connected with the experimental technique and the specific crystalline forms of molecules. It is known that SLE experiments are quite difficult to carry out. Results depend on the procedure (heating or cooling) or, for example, on the thermal histories of the materials. When studying transitions, these may be triggered by nonhomogeneous nucleation.<sup>47</sup> Despite this, substances with long chains or complicated ring structures may present different phases. For example, *n*-alkanes or *n*-alkanols may transform to a rotator phase before melting (usually termed  $\alpha$  phase).<sup>48</sup> The  $\alpha$  form is somewhat transparent and, after it cools further, changes to the more opaque  $\beta$  or  $\gamma$  forms.<sup>49,50</sup> The  $\beta$  form is a monoclinic phase with chains nearly vertical to the basal plane, while the  $\gamma$  form chains are tilted from the basal plane normal. The term “rotator phase” is due to the lack of long-range order in the rotational degrees of freedom of the molecules about their long axes. These forms are weakly ordered plastic crystalline phases between the highly ordered crystalline phases of the alkanes and their liquid phase. They are layered with long-range positional order of the molecules in three dimensions.<sup>51</sup> The most important properties are as follows: (i)

there are several rotator phases with different degrees of order; (ii) the molecules are making active rotation around and translation along the molecular axes; (iii) relatively long chain paraffins show conformational deviations from the ordered planar structure. It is no doubt that for our [C<sub>12</sub>mim][Cl] IL some of these features may be expected. Other work on alkane mixtures can also be cited,<sup>52</sup> where authors often assume untitled structures even when the pure compounds are tilted. It is also known that the transition temperature from a rotator phase to a fully crystalline state is depressed in a mixture. Typically, this has been associated with local fluctuations of the lower temperature order parameter in the higher temperature phase. When analyzing (C<sub>23</sub> + C<sub>28</sub>) the *n*-alkanes mixture (and other similar *n*-alkanes solutions) from X-ray scattering, it was concluded that while there is only long-range positional order of the density normal to the layers, there is only short-range positional order in the plane of the layers. This phase has the symmetry of a smectic liquid crystal, not previously observed in normal alkanes. In view of these literature studies, it can be possible to conclude that solid–solid phase transitions of [C<sub>12</sub>mim][Cl] may be affected by the presence of the solvent. In other words, it is possible that the transitions observed during the solubility measurements are not those encountered in pure IL, but some of the different rotator phases are involved. X-ray studies are needed in order to clarify that point.

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

$$-\ln x_1 = \frac{\Delta H_{m1}}{R} \left( \frac{1}{T_1} - \frac{1}{T_{m1}} \right) + \frac{\Delta H_{trI}}{R} \left( \frac{1}{T_1} - \frac{1}{T_{trI}} \right) + \frac{\Delta H_{trII}}{R} \left( \frac{1}{T_1} - \frac{1}{T_{trII}} \right) - \frac{\Delta C p_{m1}}{R} \left( \ln \frac{T_1}{T_{m1}} + \frac{T_{m1}}{T_1} - 1 \right) + \ln \gamma_1 \quad (1)$$

where  $x_1$ ,  $\gamma_1$ ,  $\Delta H_{m1}$ ,  $\Delta C p_{m1}$ ,  $T_{m1}$ , and  $T_1$  stand for mole fraction, activity coefficient, enthalpy of fusion, difference in solute heat capacity between the solid and the liquid at the melting point, melting point of the solute (1), and equilibrium temperature, respectively. Also,  $\Delta H_{trI}$ ,  $\Delta H_{trII}$ , and  $T_{trI}$ ,  $T_{trII}$  stand for enthalpies of transition and transition temperatures of the solute, respectively. The solubility equation for temperatures below that of the phase transition must include the effect of the transition. Equation 1 may be used assuming the simple eutectic mixtures with full miscibility in the liquid and immiscibility in the solid phases. The additional DSC experiment was investigated for the six binary mixtures of {[C<sub>12</sub>mim][Cl] + *tert*-butyl alcohol}, as an example of mixtures that are under the investigation. The possibility of the solid solution formation was tested. The DSC diagrams for the solute mole fractions range from 0 to 0.15 and from 0.7 to 1 and show immiscibility in the solid phase.

In this study, three methods are used to derive the solute activity coefficients  $\gamma_1$  from the so-called correlation equations that describe the Gibbs excess free energy of mixing ( $G^E$ ), the Wilson,<sup>53</sup> UNIQUAC ASM,<sup>54</sup> and NRTL.<sup>55</sup> The root mean square deviation of activity ( $\sigma$  defined by eq 2) was used as a measure of the goodness of the solubility correlation.

$$\sigma = \left( \sum_{i=1}^n \frac{((\ln \gamma_i^{exp}) - (\ln \gamma_i^{cal}))^2}{n-2} \right)^{1/2} \quad (2)$$

where  $(\ln \gamma_i)^{exp}$  and  $(\ln \gamma_i)^{cal}$  are, respectively, the experimental and calculated logarithm of activities of the  $i$ th point,  $n$  is the number of experimental points (including the melting point), and 2 is the number of adjustable parameters.

The calculations with the UNIQUAC ASM and NRTL models were carried out by the use of a data set of association for alcohols presented in our previous work.<sup>30</sup> None of these models correlate the data successfully, inherently because the solute is a very complicated and highly interacting molecule. For every system presented in this work, the description of SLE was given by the average standard mean deviation ( $\sigma$ ) equal from 7 to 30, which is an unexpectedly poor result. The results of correlations of imidazole in aliphatic alcohols ( $C_3$ – $C_{12}$ ) with respect to the occurrence of the alcohols association have presented much better deviations,  $\sigma = 0.98$  and  $\sigma = 1.17$  for NRTL and UNIQUAC ASM, respectively.<sup>30</sup> This is the evidence that an untypical shape of liquidus curve and high enthalpy of first ( $\alpha_1 \rightarrow \beta_1$ ) solid–solid phase transition influence the possibility of correlation.

### Concluding Remarks

The phenomenon of the four solid–solid phase transitions for  $[C_{12}mim][Cl]$  IL has been observed. The solubility of  $[C_{12}mim][Cl]$  in alcohols decreases with increasing molecular weight of an alcohol. The solubility of  $[C_{12}mim][Cl]$  in water is lower than that in alcohols ( $C_1$ – $C_8$ ) and higher than in 1-decanol and 1-dodecanol.<sup>56</sup> The use of the Pitzer activity coefficient models that account for the electrolyte nature of concentrated solutions may be used in the future and maybe will present better fitting of the experimental results.

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