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# Studies on an ionic liquid prepared from $InCl_3$ and 1-methyl-3-butylimidazolium chloride

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## Abstract

The phase diagram of the system $InCl_3$/1-methyl-3-butylimidazolium chloride (MBIC) was constructed by DSC method. A clear colorless and transparent ionic liquid was experimentally observed in $InCl_3$/MBIC system with about mole fraction of $InCl_3$ $x = 0.50$ at ambient temperature. Both Raman scattering and ab initio calculations indicate that $InCl_4^-$ is the predominant indium-containing species in this liquid.

*Keywords:* Raman scattering; Ab initio; Ionic liquid; DSC; $InCl_3$; MBIC

## 1. Introduction

Room temperature ionic liquids (RTIL), which consist solely of ions and often melt below 373 K, are a class of compounds that are being extensively studied because of their unusual properties. In particular, these liquids have very low vapor pressures. Thus, they have great potential as "green" solvents for industrial processes [1–3]. This potential is being explored vigorously as recent publications hint at their use in many typical chemical reactions. It has been shown that liquid/liquid extraction may be carried out with one of the phases being an ionic liquid [4]. Freidel-crafts reactions have been carried out with both organic [5] and organometallic substrates [6].

In addition, the initial interest in room temperature ionic liquid was due to their use as solvents for electrochemical studies [7]. In particular, the introduction of the ionic liquid prepared from $AlCl_3$/EMIC makes it possible to obtain a very large electrochemical window [8] which provide a great potential for electrodeposition of some metal alloys. By variation of the ratio of EMIC to $AlCl_3$, the relative Lewis acidity and the viscosity of ionic liquid may be altered. When the mole ratio of $AlCl_3$/EMIC exceeds 1/1, the complex anion $[Al_2Cl_7]^-$ forms and the solvent is Lewis acidic. When there is an excess of EMIC, free $Cl^-$ exists and solvent is basic in the Lewis sense. In fact, free $AlCl_3$ is not found in significant amounts in these liquids. Aluminum has been observed as $[AlCl_4]^-$ and $[Al_2Cl_7]^-$ and higher order complexes have been hypothesized. These systems have been characterized by Raman scattering [9] and electrochemical [10] means. Molecular modeling has been used to help predict the structures of the components in the ionic liquid [11]. To expand our knowledge of RTIL chemistry and because of our interest in the chemistry of indium [12,13], we decided to determine whether similar salts could be prepared by replacing $AlCl_3$ with $InCl_3$. There are limited number of reports of ionic liquids based on metals other than aluminum [14,15]. In this paper, we report that such an ionic liquid has been prepared by directly mixing $InCl_3$ and 1-methyl-3-butylimidazolium chloride under inert atmosphere. Both Raman scattering and ab initio calculations indicate that $InCl_4^-$ is the predominant indium-containing species in the liquid. Thus, we can predict that it has the great potential for electrodeposition of compound semiconductor contained indium.

## 2. Experimental

### 2.1. Chemicals

Anhydrous $InCl_3$ whose purity is 0.9999, was obtained from In-Tai Sci. Tech. Co. Ltd. of Liuzhou (PRC) and used without further purification. The 1-methylimidazole which is AR grade reagent obtained from ACROS and chlorobutane of AR grade reagent obtained from Beijing Chemicals Co.

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were used as received. Ethyl acetate and acetonitrile were distilled and then stored over molecular sieves in tightly sealed glass bottles, respectively.

### 2.2. Preparation of 1-methyl-3-butylimidazolium chloride

1-Methyl-3-butylimidazolium chloride was synthesized by refluxing the 1-methylimidazole with a large excess of the chlorobutane for 24 h. The excess chlorobutane was removed by evaporation and crude product was recrystallized from acetonitrile/ethyl acetate. The resulting white precipitate was isolated by filtration and then dried in vacuo for 24 h. The melting point is 66–68 K ($T - 273$). NMR spectrum is in good agreement with the literature [16].

### 2.3. Preparation of ionic liquid

All glasswares that contacted the room temperature ionic liquids were cleaned in hot dilution nitric acid and rinsed, respectively, in doubly deionized water, and then were baked dry in 393 K oven and stored in desiccators before use.

The ionic liquids over whole range compositions, that is, $InCl_3$ mole fraction in the mixtures $x = 0.10$, 0.15, 0.20, 0.25, 0.30, 0.33, 0.35, 0.40, 0.43, 0.45, 0.50, 0.55, 0.58, 0.60, 0.65, 0.67, 0.70, 0.75, 0.80 were prepared by simple addition of $InCl_3$ into MBIC in a dry nitrogen atmosphere glovebox. For some samples, $InCl_3$ was added slowly with stirring in a small glass beaker containing MBIC. A few of samples which were not liquid at ambient temperature were carefully heated with stirring until they were liquefied. About 10 mg samples were stored in a desiccator filled with dry nitrogen.

### 2.4. DSC procedure

The differential scanning calorimetry (DSC) experiments used a Rigaku Thermoflex DSC 8131 unit and thermal analysis station TAS100. DSC traces typically scanned from 213 to 433 K. Each sample was allowed to equilibrate for several minutes at 213 K before the scan was initiated. All scans were done using increasing temperature only and were highly reproducible. As example, Fig. 1 shows DSC trace for $x = 0.25$ mixture of $InCl_3$/MBIC. Each peak of DSC traces means a transition temperature of $InCl_3$/MBIC mixture with given compositions.

### 2.5. Raman scattering

All Raman spectra were measured on a Microscopic Confocal Raman Spectrometer (RM2000) produced by Renishaw. Laser excitation was provided by HeNe laser and was passed through a line filter and a cylindrical lens and was focused onto NMR tube containing the sample. The laser power at the sample was approximately 2 mW. Scattered light was collected at 90° from the excitation beam. The light was dispersed via an 1800 line/mm grating and detected via a liquid nitrogen cooled CCD.

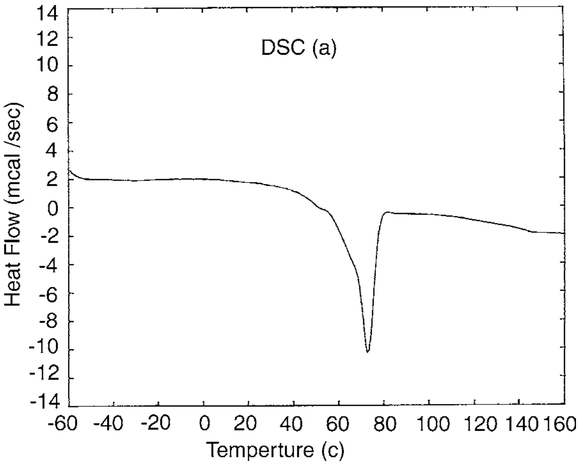

Fig. 1. DSC trace for $InCl_3$/MBIC, $x = 0.25$. The heating rate was $10\,K\,min^{-1}$. Sample sizes were ca. 10 mg.

### 2.6. Computational method

Ab initio Hartree-Fock calculations were performed to predict the structures, energies, and vibrational (Raman) frequencies of indium chloride complexes with 3–21 G* basis set. All computations were employed with GaussNet 2000.

## 3. Results and discussion

Each peak of DSC traces means a transition temperature of the $InCl_3$/MBIC mixtures. All transition temperatures corresponding with the peaks of DSC traces are listed in Table 1.

Fig. 2 is the phase diagram drawn according to Table 1 in which $x$ means mole fraction of $InCl_3$ in $InCl_3$/MBIC binary system. In Fig. 2 C is a compound, which chemical composition is $[BMI_3][InCl_6]$, with congruent melting point. $F$ is a compound, which chemical composition $[BMI_2][InCl_5]$, with incongruent melting point. $J$ is a “eutectic point”.

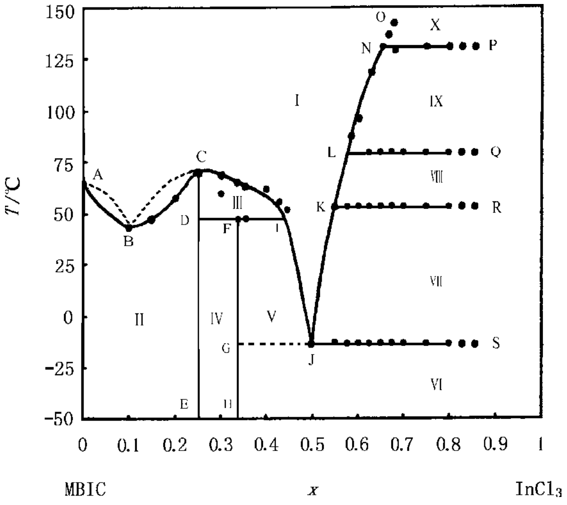

Fig. 2. The phase diagram of $InCl_3$/MBIC system.

Table 1
Peak temperature of DSC curve in different compositions ($x$) of $InCl_3$/MBIC system

| | $x = 0.00$ | $x = 0.10$ | $x = 0.15$ | $x = 0.20$ | $x = 0.25$ | $x = 0.30$ | $x = 0.33$ | $x = 0.35$ |
|---|---|---|---|---|---|---|---|---|
| First peak | 66.8 | 45.3 | 46.1 | 58.0 | 72.7 | 70 | 47.2 | 66.6 |
| Second peak | | | | | | 59 | | 48.2 |
| | $x = 0.40$ | $x = 0.43$ | $x = 0.45$ | $x = 0.50$ | $x = 0.52$ | $x = 0.55$ | $x = 0.58$ | |
| First peak | 68.7 | 66.3 | 51.2 | −15.2 | −15.2 | 53.2 | 90 | |
| Second peak | | | | | | −12.8 | −14.0 | |
| | $x = 0.60$ | $x = 0.63$ | $x = 0.65$ | $x = 0.67$ | $x = 0.70$ | $x = 0.75$ | $x = 0.80$ | |
| First peak | 98 | 121.1 | 129.2 | 128.3 | 126.8 | 129.5 | 130 | |
| Second peak | 55.2 | 79.2 | 78.1 | 80.7 | 77.3 | 82.7 | 101.6 | |
| Third peak | −13.5 | 52.8 | 53.5 | 53.6 | 53.4 | 53.6 | 82.8 | |
| Fourth peak | | −13.5 | −13.2 | −13.0 | −13.5 | −13.6 | 53.1 | |
| Fifth peak | | | | | | | −13.4 | |

Raman number I means liquid area, II means a solid solution with (BMIC + C), III means C + liquid, IV means a solid phase with (C + F), V means (F + liquid), VI means solid phase with ($F$ and $InCl_3$), VII, VIII, IX and X mean a mixture of (liquid + $InCl_3$ with different crystal). From the phase diagram, there is a narrow area of liquid phase at about $x = 0.50$ and liquid down to 258 K, that is, a colorless, transparent and mobile liquid was observed in experiments. Since there was only a peak on DSC trace in $x = 0.50$ $InCl_3$/MBIC system, it can be recognized that a pure ionic compound which might be $[MBI]^+[InCl_4]^-$ was formed. The first obvious difference between Fig. 2 and the phase diagram of $AlCl_3$/EMIC system [14] is different composition range of this liquid. While the $AlCl_3$/EMIC system is liquid at room temperature over the range 2/1 to 1/2 (mol/mol) ratio, the $InCl_3$/MBIC system is only a room temperature liquid near about $x = 0.50$, that is, there is a very narrow composition range with a liquid phase at ambient temperature. Those samples contained less than $x = 0.40$ were not homogeneous liquids at room temperature. We have not been able to prepare any homogeneous samples with $x > 0.60$ under condition where we were confident in the integrity of the same. However, the phase diagram of $AlCl_3$/EMIC system obviously shows that when $AlCl_3$ and EMIC were mixed in 1/1 mole ratio, a stable compound with higher melting point 281 K [17] was formed and it could be imaged as $[EMI]^+[AlCl_4]^-$, an ionic compound; however in the $InCl_3$/MBIC system a stable compound with higher melting point 345 K appeared at $x = 0.25$ and its anion maybe $[InCl_6]^{3-}$. The existence of this stable compound was confirmed by only one peak on the DSC trace (see Fig. 1).

If it is defined that temperature difference between 373 K and the lowest temperature at which the liquid phase exists is the depth of RTIL. The greater the depth of RTIL, the better the property of RTIL. The depth of RTIL of the $InCl_3$/MBIC system is 115 K, however, the depths are 75 K in $InCl_3$/EMIC system [18] and 50 K in $InCl_3$/BPC system [19], respectively. The variation of the depths is dependent on the structural symmetry of cation of RTIL: the more symmetric, the less depth of RTIL. Since symmetry of $[BMI]^+$ is the least among the three of cations $[BMI]^+$, $[EMI]^+$ and $[BP]^+$, depth of its RTIL is the biggest.

### 3.1. Ab initio calculation and Raman spectrum

A Hartree-Fock (RHF) geometry optimization of $[InCl_4]^-$ found the most stable structure to be a tetrahedral complex with In–Cl bond length of 2.423 Å. Table 2. lists calculated energy, bond length and structures for complexes contained trivalent indium. For $[InCl_4]^-$, calculations give four main Raman-active modes: an $E$ mode at 96.8 $cm^{-1}$ (1.8598), a $T_2$ at 116.3 $cm^{-1}$ (1.5752), an $A_1$ at 321.5 $cm^{-1}$ (8.9091) and a $T_2$ at 341.9 $cm^{-1}$ (1.5602). The numbers in the brackets are Raman scattering activity. The calculated Raman activity of the $A_1$ mode is approximately six times of the activity of the $T_2$ mode. The experimentally determined Raman spectrum of the low-wave number range of the ionic liquid of $InCl_3$/MBIC system with $x = 0.50$ is shown in Fig. 3. The

Table 2
Results of ab initio calculations for indium chloride complexes

| Species | $R$ (Å) | $E$ (hartree) | Calculated frequency (activity) ($cm^{-1}$) |
|---|---|---|---|
| $InCl_4^-$ | 2.423 | −7545.1542647 | $E$: 96.8100 (1.8598)<br>$T_2$: 116.2740 (1.5752)<br>$A_1$: 321.5256 (8.9091)<br>$T_2$: 341.8853 (1.5602) |
| $InCl_6^{3-}$ | 2.639 | −8459.79864212 | $E_g$: 119.5753 (3.7038)<br>$B_{2g}$: 119.7205 (3.7047)<br>$A_{1g}$: 143.5477 (1.5010)<br>$B_{1g}$: 144.3270 (1.5025)<br>$A_{1g}$: 219.9294 (21.6954) |
| $In_2Cl_7^-$ | 2.567<br>2.393<br>2.385<br>2.382 | −14632.7789219 | $B_2$: 46.2537 (2.1892)<br>$A_1$: 63.9602 (2.6982)<br>$A_1$: 93.9000 (2.9472)<br>$B_1$: 106.0563 (2.1080)<br>$A_1$: 111.8191 (2.7680)<br>$A_1$: 193.4499 (3.7330)<br>$A_1$: 324.6712 (35.6823)<br>$A_2$: 353.0935 (4.8351)<br>$B_1$: 355.0294 (3.3730)<br>$A_1$: 363.2470 (6.0248) |

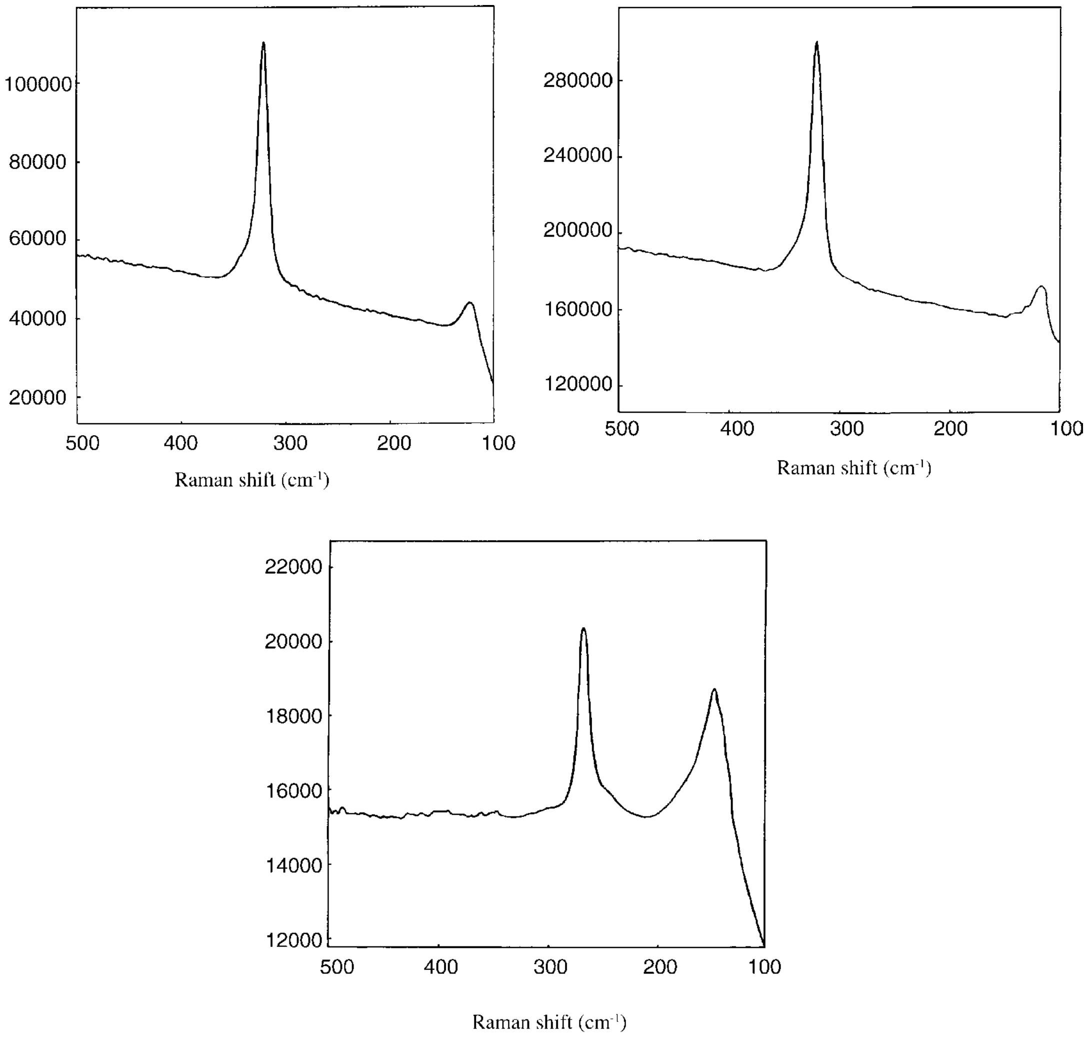

Fig. 3. Low-energy Raman spectrum of $InCl_3$/MBIC ionic liquid: $x = 0.50$ (upper left); $x = 0.60$ (upper right); $x = 0.25$ (bottom).

primary feature is a band with maximum at 321.4 cm$^{-1}$ and a feature at 121.7 cm$^{-1}$. The first feature is $A_1$ vibration for the species, while the 121.7 cm$^{-1}$ feature is the $T_2$ vibration. The calculated frequency 341.9 cm$^{-1}$ does not appear experimentally because its Raman activity is very weak and may be overlapped by the 321.5 cm$^{-1}$ feature. These Raman experimental results mean that only an anion $[InCl_4]^-$ exists in the liquid at $x = 0.50$ and it could also be confirmed by the DSC trace for $x = 0.50$ $InCl_3$/MBIC system for which there is only a peak. More importantly, it is noted that our results are in good agreement with experimental data from the literature [20].

In the same region of the spectrum, the $AlCl_3$/EMIC system shows bands at 310 and 347 cm$^{-1}$ when excess $AlCl_3$ is present [18]. The feature at 347 cm$^{-1}$ has been attributed to the $A_1$ vibration of the tetrahedral $[AlCl_4]^-$, while the feature at 310 cm$^{-1}$ is due to the presence of $[Al_2Cl_7]^-$. In the aluminum case, there is an increase in the ratio the 310/347 bands as the amount of $AlCl_3$ exceeds that of EMIC [21]. It is shown that the following association reaction may occur $[AlCl_4]^- + [AlCl_3] = [Al_2Cl_7]^-$ with an excess of $AlCl_3$.. In our case, the Hartree-Fock geometry optimization of the analogous dinuclear indium complex finds a structure which is predicted to consist of two tetrahedra with a shared central, bridging chlorine. This geometry is consistent with one of the aluminum system. Vibrational calculations for $[In_2Cl_7]^-$ predict numerous Raman feature between 46.3 and 363.2 cm$^{-1}$, which are listed in Table 2. but these vibrational frequencies were not observed. The experimentally determined Raman spectrum of $InCl_3$/MBIC system with $x = 0.60$ is shown in Fig. 3 (upper right). The primary feature is a band with maximum at 322.0 cm$^{-1}$ and a feature at 118.0 cm$^{-1}$. Since Fig. 3 upper right is almost consistent with Fig. 3 upper left, the primary feature in both figures may be attributed to $[InCl_4]^-$. It is clear that $[In_2Cl_7]^-$ does not exist in appreciable amounts in our room temperature ionic liquid. This result is consistent with phase diagram (Fig. 2) in which species contained $[In_2Cl_7]^-$ does not exist. It is shown that system of $InCl_3$/BMIC is different from $AlCl_3$/EMIC system, that is, association reaction $[InCl_4]^- + InCl_3 = [In_2Cl_7]^-$ may not occur.

The geometry optimization of $[InCl_6]^{3-}$ found the most stable structure to be a octahedra complex with In–Cl bond length of 2.639 Å. For $[InCl_6]^{3-}$, ab initio calculations give five Raman-active modes (see Table 1): $A_{1g}$ mode at 219.9 cm$^{-1}$ and $A_{1g}$ mode at 143.5 cm$^{-1}$ and $B_{1g}$ mode at 144.3 cm$^{-1}$. The calculated Raman activity of the $A_{1g}$ mode is approximately six times of the activity of $E_g$ mode and $B_{2g}$ mode. The experimentally determined Raman spectrum of the low-wave number range of the $InCl_3$/MBIC system with $x = 0.25$ is shown in Fig. 3 (bottom). The primary features are two separated bands with maxima at 148.9 and 268.1 cm$^{-1}$, respectively. The two are the $A_{1g}$ and $B_{1g}$ vibration for the species, $[InCl_6]^{3-}$, respectively. Raman spectrum and ab initio calculation further confirm that a stable compound on the phase diagram with $x = 0.25$ may exist.

In summary, we have extended the variety of possible room temperature ionic liquid by preparing a mixture with $InCl_3$ and MBIC and from Raman spectra, we have found that: (1) at the molar ratios of $InCl_3$/MBIC of 1/3 (that is $x = 0.25$) association reaction $InCl_3 + 3Cl^- = [InCl_6]^{3-}$ may occur; (2) at around $x = 0.5$, major equilibrium is $InCl_3 + Cl^- = [InCl_4]^-$, so that $InCl_4{}^-$ is primary anion in the liquid.

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