# Polymorphous crystals from chlorozincate-choline chloride ionic liquids in different molar ratios

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## Abstract

Polymorphous crystals of chlorozincate-choline chloride ionic liquid (IL) in different molar ratios were incubated at $5\,^{\circ}C$ and characterized by X-ray diffraction (XRD), differential scanning calorimeter (DSC) and optical microscope (OM). It is clearly shown that the properties of IL crystal change significantly with $X(ZnCl_2)$ (mole fraction of $ZnCl_2$) over the range from 0.67 to 0.40. Crystal (**a**) (m.p. $45\,^{\circ}C$) is formed at $X(ZnCl_2) = 0.67$, both crystal (**a**) and crystal (**b**) (m.p. $85\,^{\circ}C$) are observed at $X(ZnCl_2) = 0.50$. However, crystal (**c**) (m.p. $27\,^{\circ}C$) and non-coordinated choline chloride are observed at $X(ZnCl_2) = 0.40$. Morphology of the IL crystal also changes greatly with the $X(ZnCl_2)$. This investigation reveals that structures and properties of the IL anions vary with the $X(ZnCl_2)$ and the molar ratio is a pivotal factor dominating the IL property.
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## 1. Introduction

Room temperature ionic liquids (ILs) have attracted more and more interest due to their unique physical and chemical properties, such as high polarity, non-coordination, non-volatility, and inflammability, etc. [1–3]. ILs are considered as the alternative of volatile organic solvents in chemical processing and extraction and have numerous potential applications in many other fields. Knowledge of the intrinsic properties of various ILs is important in applications. Although ILs in the molten state have been studied widely by many conventional methods, hitherto now, very few are known about the crystals of ILs [4–12]. Study of IL crystals is an interesting subject itself and such information may provide more insights into the understanding of structures and characters of ILs. Crystal structure of a prototype IL, 1-*n*-butyl-3-methylimidazolium chloride [bmim]Cl has previously been studied [4–7]. Holbrey et al. [4]

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found that the [bmim]Cl has orthorhombic (1) and monoclinic (2) crystals; the monoclinic crystal can be gained only via crystallization with other solvent or solute species present. The authors also observed the coexistence of two structures of [bmim]$^+$ cations in the molten state by X-ray diffraction (XRD) and Raman spectroscopy. Saha et al. [5,6] and Ozawa et al. [7] also independently confirmed the formation of crystals (1) and (2) in a similar manner. Nishikawa et al. [8] further studied the structure of IL 1-*n*-butyl-3-methylimidazolium iodide [bmim]I by wide-angle X-ray scattering (WAXS) and Raman spectroscopy; they found that the cation structures in the liquids of [bmim]I, [bmim]Cl and [bmim]Br are similar to them in the crystals and the anions have long-range correlation. Hardacre et al. [9] investigated the structure of molten and crystallized dimethylimidazolium chloride using neutron diffraction for the first time and found significant charge ordering present in the liquid, closely resembling that in the solid state. In all above studies, hydrogen bonding (C–H $\cdots$ X, X = O, Cl) was recognized as an important role in constructing the IL structures. More recently, Dronskowski et al. [10,11] investigated the hydrogen bonding in crystals of a series of alkyl-substituted imidazolium cation based ILs; they found that the hydrogen bonding, if present, is the most important contribution to the lattice energy in ILs.

ILs based on metal salts are also important in application and chloroaluminate melts have been industrially applied for a long time. The high water sensitivity of chloroaluminate ILs hinders its wide application. It has recently been shown that ILs can be formed using $ZnCl_2$ with pyridium [12], imidazolium salts [13,14], or quaternary ammonium salts (QAS) such as choline chloride [15]. The $ZnCl_2$-QAS ILs are easy to prepare and relatively water and air stable, their low cost enables their use in large-scale applications, e.g. zinc and zinc alloy deposition, batteries. We have also recently reported the radiation-induced polymerization of vinyl monomers in $ZnCl_2$–[$Me_3NC_2H_4OH$]Cl (ChCl–$ZnCl_2$) IL in a 2:1 molar ratio [16,17], and found much higher conversion rate of monomer and molecular weight of resulting polymer in comparison with conventional solvents.

Very recently, Abbott et al. [18] measured the freezing point and ionic species distribution of the ChCl–$ZnCl_2$ IL at 60 °C as a function of composition. In order to obtain more information about the chemistry of the ChCl–$ZnCl_2$ IL, in this work, we made an attempt to grow crystals of this IL in different compositions and analyzed their properties by XRD, differential scanning calorimeter (DSC), and ATR-IR. Our preliminary results reveal that the molar ratio of two components has a significant effect on morphology and melting point of the IL crystals. Such information is in turn useful for understanding of the chemistry of the molten IL.

## 2. Experimental procedure

### 2.1. Materials

The ChCl–$ZnCl_2$ IL is prepared according to the method reported by Abbott et al. [15]. Three kinds of ILs are prepared at $X(ZnCl_2) = 0.67$, 0.50 and 0.40, corresponding to the mixture in molar ratios of 2:1, 1:1 and 2:3, respectively. All chemicals used are of analytical grade and purchased from Acros Corporation. After removing the volatile impurities (water, etc.) by evaporation under vacuum at 100 °C over night, the ILs sealed in airtight glass tubes were incubated at 5 °C for 7–20 days to prepare the crystals.

### 2.2. Methods

The crystal structures were characterized by XRD (B/max 2550A, Rigaku Corp.) with mono-chromatized Cu-K$_\alpha$ radiation at a scan rate of 0.1° $2\theta \, s^{-1}$. The melting points and transition heats of crystals were determined by DSC (DSC-822e, Mettler-Toledo Corp.). The sample was scanned from −20 to 100 °C at a programmed rate of 10 °C/min, using indium to calibrate the temperature and heat flow of the DSC equipment. Crystal morphology was observed by polarized optical microscopy (POM) (BH-2, Olympus Corp.) equipped with a high-resolution CCD camera. Chemical structures of the solid surface of the crystals were detected by attenuation total

reflection infrared spectroscopy (ATR-IR) (Avatar 360, Nicolet Co. Ltd.).

## 3. Results and discussion

### 3.1. DSC measurement and XRD pattern

The ChCl–ZnCl$_2$ IL was innovated by Abbott et al. [15] and they found that the heating of mixtures of ZnCl$_2$ and choline chloride over a range of $X$(ZnCl$_2$) (0.50–0.75) can form colorless IL, with the freezing points varying from ca. 65 °C ($X$(ZnCl$_2$) = 0.50) to 25 °C ($X$(ZnCl$_2$) = 0.67) and 45 °C ($X$(ZnCl$_2$) = 0.75). We found on occasion that this IL can form crystal by long-time incubation at low temperature, and such a crystal has different morphology with the change in composition. Here we prepared three kinds of ChCl–ZnCl$_2$ IL at $X$(ZnCl$_2$) = 0.67, 0.50 and 0.40. The crystallization of IL is slow and difficult, especially for the IL at $X$(ZnCl$_2$) = 0.67 and 0.50. However, once formed, the crystals are stable below 15 °C. Figs. 1 and 2 show the DSC curves and XRD patterns of the three IL crystals. Fig. 1(a) illustrates only one melting peak at 45 °C in the DSC curve for the IL crystal (**a**) at $X$(ZnCl$_2$) = 0.67. The XRD pattern of crystal (**a**) (see Fig. 2(a)) has three diffraction peaks at $2\theta = 10.60°$, 21.3° and 27.6°, with relative peak area of 100, 62 and 6.6, respectively. At $X$(ZnCl$_2$) = 0.50, the DSC curve shows two distinct melting peaks: one is at the same position ($T_m = 43$ °C) of crystal (**a**) and the other appears at 85 °C. The second one is assigned to crystal (**b**). The XRD pattern (see Fig. 2(b)) also confirms the formation of crystals (**a**) and (**b**). Crystal (**b**) has diffraction peaks at $2\theta = 18.5°$, 32.7° and 37.4° with relative peak area of 18.9, 93.3 and 100, respectively. It is clear that these two crystals have a common diffraction peak at 21.4°. By decreasing the $X$(ZnCl$_2$) to 0.40, the DSC curve of crystal (**c**) shows a new melting peak at 27.0 °C, no other peak appears in a scan of the temperature up to 200 °C. In a parallel experiment, we found that the mixture is partially in the molten state; a lot of white particles still exist even by raising the temperature to 200 °C. The XRD pattern (see Fig. 2(c)) reveals the existence of [Me$_3$NC$_2$H$_4$OH]Cl solid ($2\theta = 22.3°$,
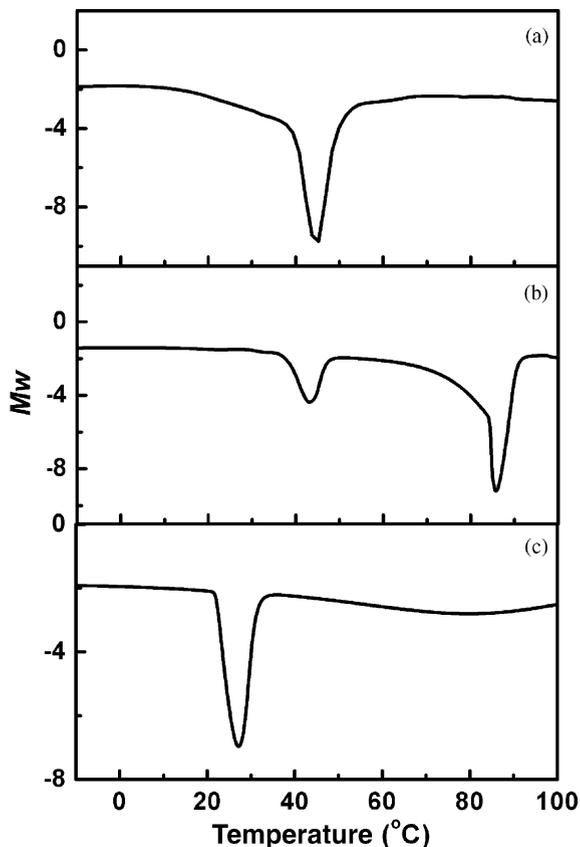


Fig. 1. DSC heating curves for ionic liquid crystals at a scan rate of 10 °C/min. $X$(ZnCl$_2$) of [ZnCl$_2$]/[Me$_3$NC$_2$H$_4$OH]Cl: (a) 0.67, (b) 0.50, (c) 0.40.

28.6°, 11.7° and 15.7°) in addition to crystal (**c**). It means that excess choline chloride remains uncoordinated in the IL. The other two peaks at $2\theta = 19.2°$ and 13.3° with relative peak area of 100 and 45 belong to the diffraction peaks of crystal (**c**). In this case, since the mole fraction of ZnCl$_2$ is much less than that of choline chloride, part of the choline chloride does not complex with ZnCl$_2$ and is present in the free state.

Melting points and enthalpies of melting transition for the IL crystals with different compositions are illustrated in Table 1. Melting points of the IL crystals are quite different from those of the ILs as measured by Abbott et al. [15], because crystals are formed only under special conditions. Based on the heats of transition for crystal (**a**) at
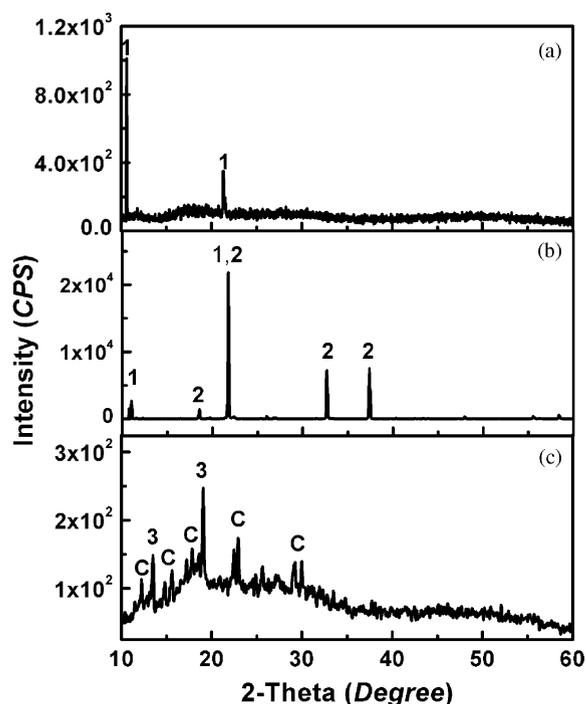
Fig. 2. XRD patterns of ionic liquid crystals. $X(ZnCl_2)$ of [ZnCl$_2$]/[Me$_3$NC$_2$H$_4$OH]Cl: (a) 0.67, (b) 0.50, (c) 0.40.

Table 1
$T_m$, heat of transition and composition of crystals calculated from the DSC curves

| Sample | $X(ZnCl_2)$ of IL | $T_m$ (°C) | $\Delta H_m$, Enthalpy of melting (J g$^{-1}$) | $X(ZnCl_2)$ of crystal |
|---|---|---|---|---|
| **a** | 0.67 | 44.72 | 35.45 | 0.67 |
| **b** | 0.50 | 42.88 | 35.45 | 0.67 |
|  |  | 85.53 | 121.23 | 0.14 |
| **c** | 0.40 | 26.99 | — | — |

$X(ZnCl_2) = 0.67$ and for two crystals at $X(ZnCl_2) = 0.50$, it is calculated that the $X(ZnCl_2)$ in crystals (**a**) and (**b**) formed at $X(ZnCl_2) = 0.50$ are 0.67 and 0.14, respectively. The weight ratio of the two crystals is 8:9. The enthalpies of melting of the two crystals are markedly different: 35.5 J g$^{-1}$ for crystal (**a**) and 121.2 J g$^{-1}$ for crystal (**b**). All these data imply that the IL at $X(ZnCl_2) = 0.50$ is actually a mixture of two different ILs. It might be natural that crystal (**b**) would coexist in the material formed at $X(ZnCl_2) = 0.40$ or crystal (**c**)

coexists in the crystal formed at $X(ZnCl_2) = 0.50$. However, this possibility is negligible on the basis of XRD pattern and DSC measurement. The IL crystal structure seems to be dominated by the acidity of the system as well as the molar ratio of ZnCl$_2$ and choline chloride.

### 3.2. Crystal morphology and ATR-IR spectra

Fig. 3 shows the optical and polarized optical micrographs of the crystals incubated from ILs at $X(ZnCl_2) = 0.67$, 0.50 and 0.40. By viewing with the microscope under normal light and cross polarized light in situ, we found that the crystals incubated from ILs are rod-like at $X(ZnCl_2) = 0.67$ (Fig. 3(a)), sheet-like at $X(ZnCl_2) = 0.50$ and 0.40 (see Fig. 3(b) and (c)). Some rod-like crystals can also be clearly identified at $X(ZnCl_2) = 0.50$.

Fig. 4 shows the ATR-IR spectra of the IL crystals. The wide strong peak at 3405 cm$^{-1}$ belongs to the stretching vibration of O–H, while the two peaks at 3208 and 3153 cm$^{-1}$ are due to the hydrogen bonding (–O–H$\cdot$X, X = Cl) according to the report by Kölle and Dronskowski [11], who systematically studied the H-bonding in ILs. Along with the change of $X(ZnCl_2)$ from 0.67 to 0.40, the peak intensity at 3208 cm$^{-1}$ decreases but that at 3153 cm$^{-1}$ increases. This opposite trend indicates a difference in crystal structure. The two peaks at 3208 and 3153 cm$^{-1}$ may be caused by different stereo-conformations of crystals and/or difference in anion size.

### 3.3. Explanation of the composition effect

In the report by Abbott et al. [15,18], FAB-mass spectra indicate the presence of three main chlorozincate anions, i.e. $ZnCl_3^-$, $Zn_2Cl_5^-$, and $Zn_3Cl_7^-$. Higher clusters were also detected but occur at very low intensities. Since Cl$^-$ is a Lewis base and chlorozincate anions are Lewis acids, the Lewis acidity/basicity of the ChCl–ZnCl$_2$ IL can be varied by altering its composition. The composition effect on the anion size and distribution may be analogous to the chloroaluminate ILs, which were previously intensively investigated. For example, the Raman [19] and NMR [20,21] spectra of the AlCl$_3$-1-(1-butyl)-pyridinium chlor-
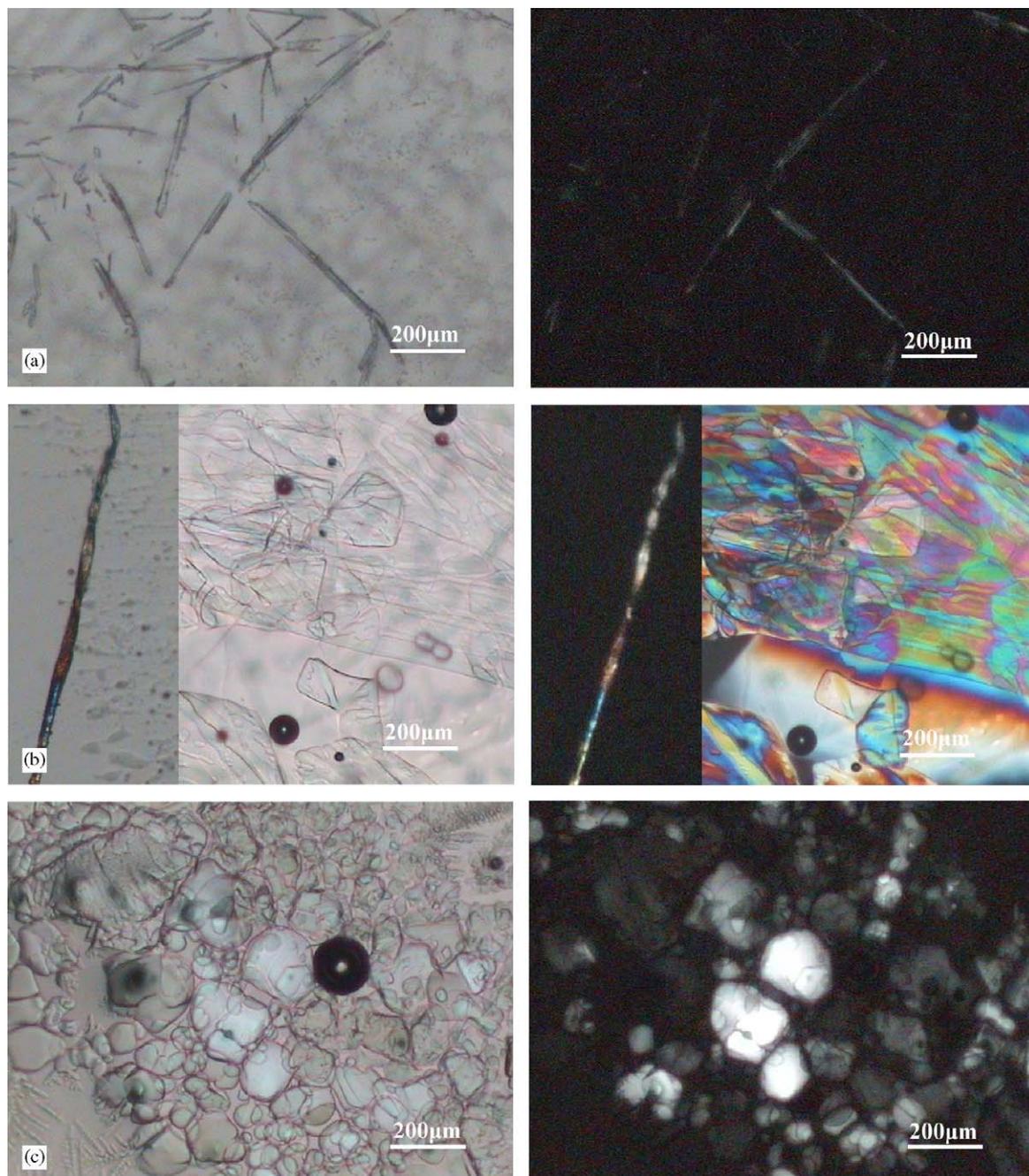
Fig. 3. Optical (left) and cross polarized optical (right) micrographs of crystals incubated from ionic liquid. $X(ZnCl_2)$ of $[ZnCl_2]/$ $[Me_3NC_2H_4OH]Cl$: (a) 0.67, (b) 0.50, (c) 0.40.

ide (BuPy) melts show that the form of chloroaluminate (III) anion varies while the mole fraction of $AlCl_3$ in the IL changes from 0.5 to 0.67.

Aluminum is present entirely in the $AlCl_4^-$ form in the basic IL ($X(AlCl_3) < 0.5$). In the acidic IL, it is present in the mixture of $AlCl_4^-$ and $Al_2Cl_7^-$ at
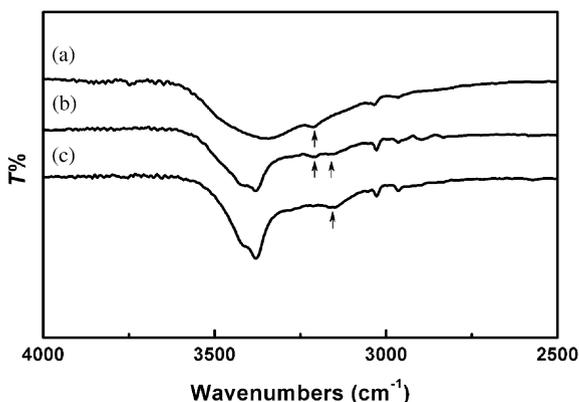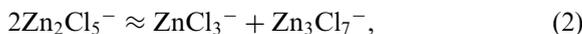
Fig. 4. ATR-IR spectra of IL crystal. $X(ZnCl_2)$ of $[ZnCl_2]/[Me_3NC_2H_4OH]Cl$: (a) 0.67, (b) 0.50, (c) 0.40.

$0.5 < X(AlCl_3) < 0.67$ and only in the form of $Al_2Cl_7^-$ at $X(AlCl_3) = 0.67$. Similarly, Abbott et al. [18] proposed Eq. (1) for the ChCl–ZnCl$_2$ IL at $X(ZnCl_2) = 0.67$ and equilibria (2) and (3) for the explanation of actual zinc anions present.

$$2ZnCl_2 + Ch^+Cl^- \approx Zn_2Cl_5^- + Ch^+, \qquad (1)$$

$$2Zn_2Cl_5^- \approx ZnCl_3^- + Zn_3Cl_7^-, \qquad (2)$$

$$Zn_2Cl_5^- \approx ZnCl_2 + ZnCl_3^-. \qquad (3)$$

The authors measured the equilibrium constant for Eq. (2) to be $2.0 \times 10^{-5}$ at 60 °C, smaller than that for the analogous chloroaluminate [22] by two orders of magnitude. Therefore, the primary zinc anion in the ChCl–ZnCl$_2$ IL is $Zn_2Cl_5^-$ with $ZnCl_3^-$ becoming more abundant in more Lewis basic solutions. The concentration of $Zn_3Cl_7^-$ is relatively small. However, temperature variation likely results in a change in the equilibrium constant, consequently, the distribution of chlorozincate ions is altered.

In our experiment, it is clear that different crystals are formed as a result of the change in $X(ZnCl_2)$. The observation of different crystals with the change of $X(ZnCl_2)$ is indicative of strong and complex interactions between choline chloride and chlorozincate anions. Both DSC and XRD measurements indicate only the formation of rod-like crystal (a) at $X(ZnCl_2 = 0.67)$, hence the actual chemical formulae of the IL can be

considered as $[Ch^+]Zn_2Cl_5^-$. At $X(ZnCl_2 = 0.50)$, both rod-like crystal (a) and sheet-like crystal (b) are observed in comparable ratio, indicating the presence of both $Zn_2Cl_5^-$ and $ZnCl_3^-$ anions. The IL actually has two components: $[Ch^+]Zn_2Cl_5^-$ with $X(ZnCl_2) = 0.67$ and $[Ch^+]ZnCl_3^-$ with $X(ZnCl_2) = 0.14$. The coordination number of ChCl around zinc $ZnCl_3^-$ in the latter is six. The measured freezing point of 65 °C [15] at $X(ZnCl_2) = 0.50$ may be due to this IL because the $[Ch^+]Zn_2Cl_5^-$ IL in the mixture has a significantly lower value. The difference between the freezing point of IL and melting point of IL crystal is 20 °C for ILs at $X(ZnCl_2) = 0.67$ and 0.50. At $X(ZnCl_2) = 0.40$, sheet-like crystal (c) and non-coordinated choline chloride are observed, in this case no $Zn_2Cl_5^-$ but $ZnCl_3^-$ is present in the IL. It is obvious that this IL differs in morphology and melting point from the $[Ch^+]ZnCl_3^-$ IL observed $X(ZnCl_2) = 0.50$, although they have the same anion, which is probably due to the difference in coordination number or in $X(ZnCl_2)$ and the process of crystallization.

## 4. Conclusion

The crystal of IL ChCl–ZnCl$_2$ has a very different property along with the change in molar ratio of the two components. Rod-like crystal (a) and sheet-like crystals (b) and (c) were observed with changing the $X(ZnCl_2)$ of IL from 0.67 to 0.40; their properties were characterized by DSC, XRD and ATR-IR. These results indicate that the interactions between choline chloride and ZnCl$_2$ is very complicated, the anion size and the coordination number of choline chloride around zinc ion play key role in controlling the properties of IL crystal or IL in the molten state.

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