

Preparation and Thermal Property of Ionic Liquid based on ZnCl₂/ChCl

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Abstract. In this study, Ionic Liquids (ILs) based on ZnCl₂/ChCl were prepared in different molar ratio (1:1, 2:1, 3:1). The structures of ionic liquids are measured by FT-IR and XRD. Thermal properties of ionic liquids, such as melting temperature, the heat of fusion and the heat of capacity, are measured by differential scanning calorimetry (DSC). Also, thermal conductivity and thermal stability were studied by Thermal Conductivity Meter, TGA. There three kinds of anions (ZnCl₃⁻, Zn₂Cl₅⁻, Zn₃Cl₇⁻) in the Ionic Liquids. With the proportion of ZnCl₂ increased, the melting point and heat of fusion change from 60.30 to 128.99 J•cm³. This deserve to the connection between Ch⁺ and different anions. The proper melting point and heat of fusion of ZnCl₂/ChCl indicates its possibility as Novel Phase Change Materials.

Keywords: Ionic liquids, thermal property, PCMs.

1. Introduction

In the past few decades, interest in the use of Phase Change Materials (PCMs) has gained momentum in the fields thermal energy storage, such as solar energy, industrial waste heat, intermittent electric heating energy and so on. [1]–[4] As we know, the qualified materials in a PCM application rely on a set of desirable thermophysical properties that includes a high heat of fusion (DHf), a phase transition temperature suited to the application, high thermal conductivity, no tendency to phase separate, good phase-change kinetics (little supercooling, sufficient crystallization rate) chemical stability, low toxicity, and low flammability. Among the most frequently used phase-change materials (PCMs) for solar heating systems are inorganic PCMs (CaCl₂•6H₂O, Na₂SO₄•10H₂O, etc.) and organic PCMs (polyethylene glycol, paraffins, amides, etc.). However, Inorganic PCMs are prone to obtain phase separation and corrosion. Organic PCMs are highly volatile and flammable. [5] Therefore, new PCMs overcoming the defects of inorganic and organic PCMs are urgently needed.

Ionic liquids (ILs)-a group of salts, which are liquid at ambient temperature (less than 100°C) and are considered as the potential replacement of the currently used working fluid. [6]–[10] ILs have several excellent physical and chemical properties including high thermal stability, negligible vapor pressure and volatility, exposure to air and moisture stability, low melting point, wide electrochemical window, nonflammability, high ionic conductivities, high solvating capability, corrosion resistance to plastics and carbon steels. [11]–[15] For those excellent properties, ILs become very useful in material processing, as a catalyst for synthesis of functional materials, and as lubricants in different areas.[16], [17]

Due to its diverse potential applications, ILs have been investigated by a number of researchers to explore different perspective of the liquid; most researches concentrated on the study of thermophysical

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properties; among those only a few numbers of study were concentrated on the study of phase-change properties. [18]–[22]

As we know, Ionic Liquids based on the NTf_2 anion have been investigated; The heats of fusion of butyltrimethylammoniumbis (trifluoromethylsulfonyl) amide ($[\text{N}_{1,1,1,4}][\text{NTf}_2]$) and 1-butyl-1-methylpyrrolidinium $[\text{NTf}_2]$ were reported to be 16 and 27 J g^{-1} , respectively. Although some of the issues of the inorganic and organic PCMs (corrosivity and flammability) are alleviated by these ionic materials, their heats of fusion and/or their melting points are impractically low. Doman' ska et al. investigated the thermophysical properties of N-hexylquinolinium NTf_2 and obtained a high heat of fusion (63.5 kJmol^{-1}) for this ionic liquid.[23], [24]

To the best of the authors, no study has been reported yet on phase-change properties and heat transfer performance of ILs based on $\text{ZnCl}_2/\text{ChCl}$. Herein, we prepared ILs based on $\text{ZnCl}_2/\text{ChCl}$ in the ratio of 1:1, 2:1, 3:1 and characterized by FT-IR and XRD. Thermal properties such as melting temperature, heat of fusion, heat of capacity and thermal conductivity were investigated. Also, the trend of thermal properties in different ratios was studied.

2. Experimental Section

2.1. Materials and method

Choline chloride ($\geq 98 \text{ wt } \%$, AR) was purchased from China National Pharmaceutical Group Corporation. Choline chloride was recrystallized in ethanol. ZnCl_2 ($\geq 99 \text{ wt } \%$, AR) was purchased from China National Pharmaceutical Group Corporation. ZnCl_2 and ChCl were dried in the drying oven to remove the absorbed water prior to use. Ionic Liquid based on $\text{ChCl}/\text{ZnCl}_2$ was synthesized as reported previously.^[25] Three kinds of ILs are prepared at $X(\text{ZnCl}_2)=0.75, 0.67$ and 0.50 , corresponding to the mixture in molar ratios of 3:1, 2:1 and 1:1, respectively. The general route for the synthesis of the ionic liquids was as follows: choline chloride was mixed with zinc chloride and heated to $150 \text{ }^\circ\text{C}$ in air with stirring until a clear colourless liquid was obtained. Then removing the volatile impurities (water, etc.) by evaporation under vacuum at $100 \text{ }^\circ\text{C}$ overnight.

2.2. Characterization

Fourier transform infrared (FTIR) spectra of the samples were obtained using a Bruker Tensor-27 FTIR spectrophotometer at a scanning number of 30 with the KBr sampling method. The crystal structures were characterized by XRD (B/max 2550 A, Rigaku Corp.) with mono-chromatized $\text{Cu-K}\alpha$ radiation at a scan rate of $0.1^\circ 2\theta \text{ s}^{-1}$. The melting points and transition heats of $\text{ChCl}/\text{ZnCl}_2$ were performed with differential scanning calorimetry (DSC), provided by Mettler Toledo. The samples inside the DSC furnace were exposed to a N_2 atmosphere. The sample was typically 6-7 mg and enclosed in an aluminum pan. The standard heating or cooling rate of the present DSC measurement was set at 2 Kmin^{-1} . The measuring temperature ranged from -20 to $100 \text{ }^\circ\text{C}$. Thermal stabilities were investigated by thermal gravimetric analysis (TGA, STA409PC, Netzsch, Germany). Samples of approximately 15 mg were heated from 20 to $700 \text{ }^\circ\text{C}$ at a rate of $10^\circ\text{C}/\text{min}$ under a constant stream of nitrogen at a flow rate of 20 ml/min . The thermal conductivity of ionic liquids were measured using a Hot Disk Thermal Constants Analyzer (TPS 2500s, Hot Disk AB, Sweden) that is based on the transient plane source (TPS) technique. A constant temperature water bath (TC-502P, Brookfield, USA) was used to control the measurement temperature with a stability of $0.01 \text{ }^\circ\text{C}$.

3. Result and Discussion

3.1. FT-IR spectra and XRD

In IR spectrum are shown in Fig.1, 1090 and 956 cm^{-1} could be assigned to C-O and C-C-O anti-symmetric stretching vibration associated with $\text{NC}_2\text{H}_4\text{OH}$ group of choline cation. The characteristic peaks for CN anti-symmetric stretching vibration could be easily found in the relatively lower bands (1037 - 1134 cm^{-1}). In addition, Peaks at 1478 , 2906 and 3018 cm^{-1} could be ascribed to the vas and vs stretching vibration $-\text{CH}_3$. 1406 and 2952 cm^{-1} refer to $\text{VsCH}_2, \text{VasCH}_2$. The bands near 3250 - 3500 cm^{-1} could be assigned to the $-\text{OH}$ part. Along with the change of $X(\text{ZnCl}_2)$ from 0.50 to $0.75 = 0.75, 0.67$ and 0.50 , the peak at 3500 cm^{-1} has little change. This may be caused by different stereo-conformations of crystals and/or

difference in anion size. As investigated by FAB-mass spectra, there three main chlorozincate anions (ZnCl_3^- , Zn_2Cl_5^- , Zn_3Cl_7^-) in this system. While equilibria 1,2 and 3 also effect the actual zinc species present.

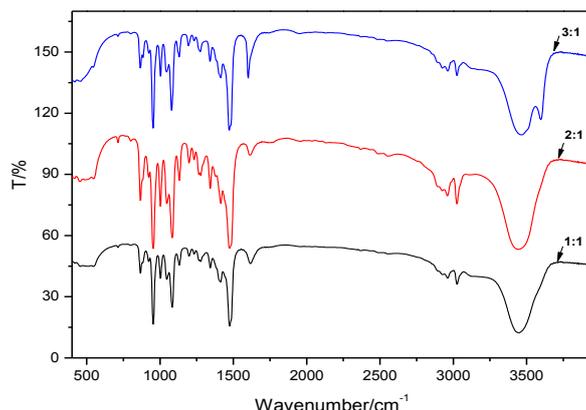


Fig. 1: IR spectra for $\text{ZnCl}_2/\text{ChCl}$



From the study of XRD, there are various Zn species in different ratios. These will affect their morphology and be reflected in XRD pattern. In previous work, as shown in Fig.2, Zou et al. employed XAFS to calculated the average coordination number and distance of Zn species at different $x(\text{ZnCl}_2)$ of ChCl-ZnCl_2 ionic liquid and a new mechanism of interactions between Ch^+ cation and Cl-Zn-Cl ion pairs or Cl^- is proposed. At $X(\text{ZnCl}_2) = 0.50$, Ch^+ cation connect with the unique ZnCl_3^- . At $X(\text{ZnCl}_2) = 0.67$, Two kinds of Zn species (ZnCl_3^- , Zn_2Cl_5^-) have special coordination number and mode. Also, Zn species and coordination modes are more complicate at $X(\text{ZnCl}_2) = 0.75$.

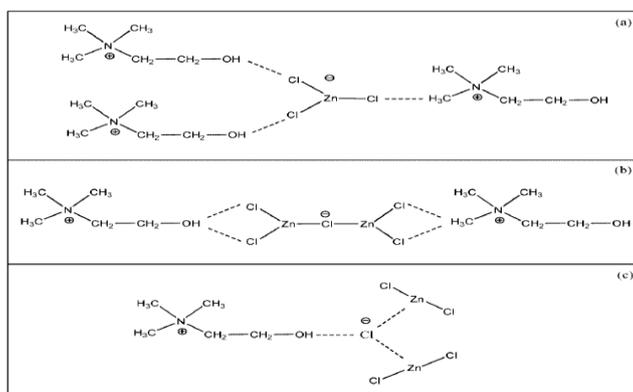


Fig. 2: Structures of the three Zn species in ChCl-ZnCl_2 ILs [26]

3.2. Thermal property

Thermal property is an important part of ionic liquids and PCMs. Variations of the energy storage properties of $\text{ZnCl}_2/\text{ChCl}$ were characterized by DSC tests. Both the melting point (onset of melting) and latent heat of fusion of $\text{ZnCl}_2/\text{ChCl}$ were extracted from the heating DSC curves. As shown in Figure 4 and Table 1, by raising the $X(\text{ZnCl}_2)$ melting point is increased from 315.0 to 362.5 K. While heat of fusion is changed by 68.69, from 60.30 to 128.99 J/cm³. Especially the heat of fusion for sample a is twice more than sample c, this may due to the compact connection between Ch^+ and ZnCl_3^- . Also, the density of ILs has same trend. Furthermore, we studied its thermal conductivity and heat of capacity at 25 °C. Its heat capacity and thermal conductivity for energy storage has certain advantages. At the same time, its thermal stability is good, it can be stable in the presence of 320 °C, which also provides the possibility of its application.

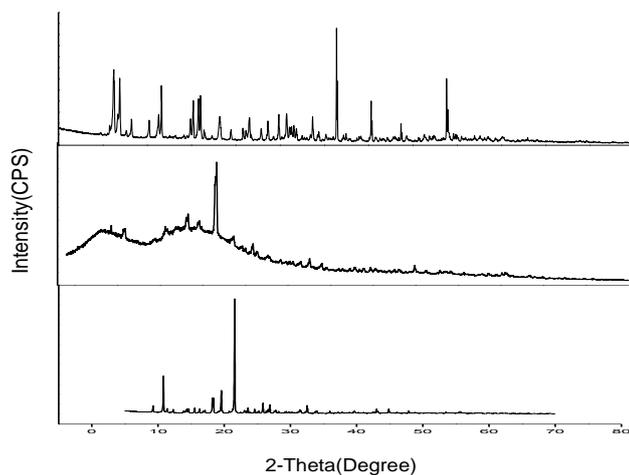


Fig. 3: XRD patterns of ZnCl₂/ChCl X(ZnCl₂): (a)0.50, (b)0.67, (c) 0.75

Table 1: Thermal properties of ZnCl₂/ChCl

| Sample | X(ZnCl ₂) | T _m (K) | ρ(g/cm ³) | Heat of fusion(J/cm ³) | Heat of fusion(J/g) | Thermal conductivity(W/m ² *K) | Heat of capacity(J/g/°C) |
|--------|-----------------------|--------------------|-----------------------|------------------------------------|---------------------|---|--------------------------|
| a | 0.50 | 362.5 | 1.517 | 128.99 | 85.03 | 0.319 | 1.405 |
| b | 0.67 | 316.0 | 1.419 | 93.13 | 65.63 | 0.341 | 1.639 |
| c | 0.75 | 315.0 | 1.359 | 60.30 | 44.37 | 0.346 | 1.630 |

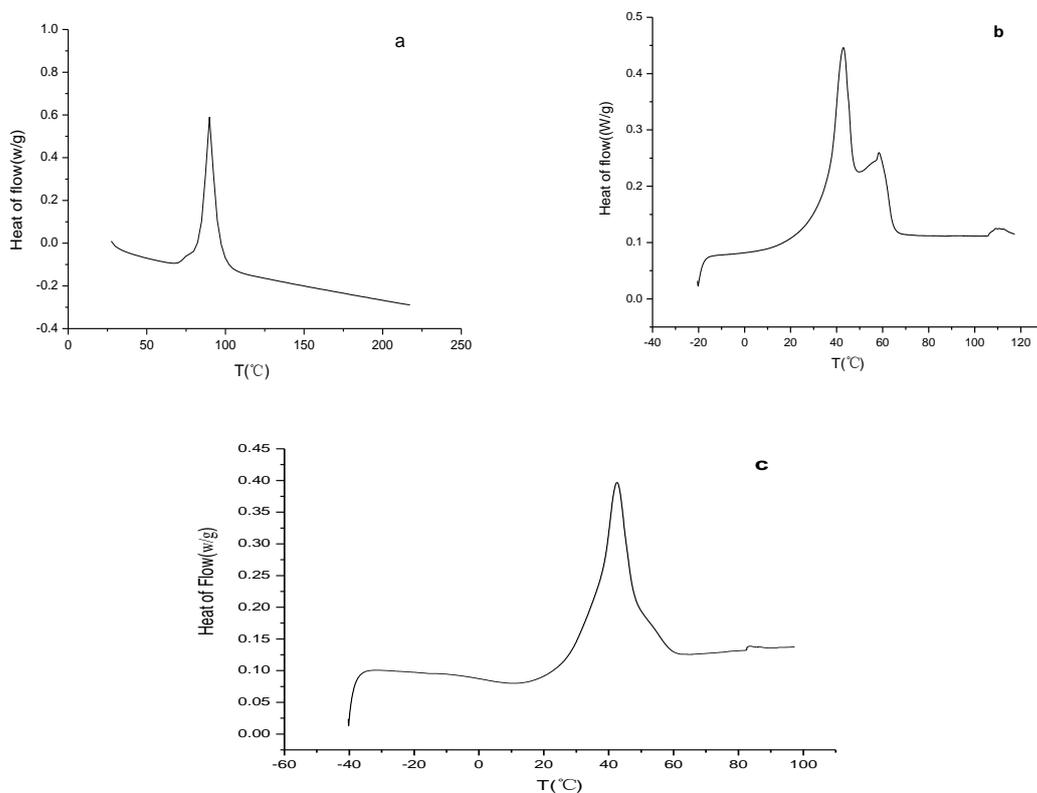


Fig. 4: DSC curve of ZnCl₂/ChCl X(ZnCl₂): (a) 0.50, (b) 0.67, (c) 0.75

4. Conclusion

In this study, we investigated the structure and thermal properties of ionic liquids based on ZnCl₂/ChCl. The proper melting point and heat of fusion of ZnCl₂/ChCl indicates its possibility as Novel Phase Change

Materials. Compared with the current pure inorganic or organic Phase Change Materials (PCMs), this new type PCMs based on organic/inorganic compound which broaden the horizon in this field. Also, we enrich the application of ionic liquids in different areas.

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6. References

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