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Journal of Crystal Growth 281 (2005) 616–622

JOURNAL OF CRYSTAL GROWTH

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

Yaodong Liu, Guozhong Wu*, Mingying Qi

Shanghai Institute of Applied Physics, Chinese Academy of Sciences, P.O. Box 800-204, Shanghai 201800, China

Received 2 February 2005; accepted 21 April 2005
Available online 31 May 2005
Communicated by K. Sato

Abstract

Polymorphous crystals of chlorozincate-choline chloride ionic liquid (IL) in different molar ratios were incubated at 5 °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 °C) is formed at $X(ZnCl_2) = 0.67$, both crystal (**a**) and crystal (**b**) (m.p. 85 °C) are observed at $X(ZnCl_2) = 0.50$. However, crystal (**c**) (m.p. 27 °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.

Keywords: A1. Crystal morphology; A1. Crystal structure; A1. Ionic liquids; B1. Zinc compounds

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]

*Corresponding author. Tel./fax: +86 21 59558905.
E-mail address: wuguozhong@sinap.ac.cn (G. Wu).

0022-0248/$ - see front matter
doi:10.1016/j.jcrysgro.2005.04.073

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 · · 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 monochromatized Cu-K_α 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