

Recovery of [BMIM]FeCl₄ from homogeneous mixture using a simple chemical method

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(Received 16 September 2009 • accepted 3 November 2009)

Abstract—[BMIM]FeCl₄ (1-butyl-3-methylimidazolium tetrachloroferrate) was successfully separated from a homogeneous mixture of [BMIM]FeCl₄ and H₂O via a simple two-step method of phase-division by adding inorganic salt plus chemical extraction, or alternatively, ultracentrifugation, or ultrastrong magnetic field. NaCl showed excellent and effective phase-dividing performance combined with chemical extraction method from the homogeneous mixture of [BMIM]FeCl₄ and H₂O lower to 1 v%.

Key words: Recovery, [BMIM]FeCl₄, Homogeneous Mixture, Chemical Method

INTRODUCTION

Room temperature ionic liquids (RTILs) have been extensively used as a reaction medium in a variety of fields due to their attractive and unique properties such as non-volatility, non-flammability, high thermal stability, high ionic conductivity and wide electrochemical potential window. In particular, as a designer solvents [1], ionic liquid (ILs) can be functionalized by altering their anions or cations; therefore, new functional ILs can be synthesized to meet the increasing demand on different properties of RTILs in various fields.

A new functional RTIL system was reported by substituting FeCl₄⁻ for Cl⁻ [2-7], and Fig. 1 shows the molecular structure of one typical FeCl₄⁻-containing RTIL, [BMIM]FeCl₄ [8-12]. The incorporation of FeCl₄⁻ ion changed the physicochemical properties of the original IL, e.g., hydrophilic 1-butyl-3-methylimidazolium chloride (BMIMCl) [13] turned into hydrophobic [BMIM]FeCl₄ [8,14]. Moreover, FeCl₄⁻ brings both strong magnetic response [3,5,15] and high oxidation ability, therefore, nano-sized conducting polymers (CPs) can be prepared [9-11] without adding additional oxidant. In addition, FeCl₄⁻-containing ionic liquid was also found to be a very efficient catalyst for some organic synthesis processes [7,8,12,16].

It is known that for the application of ILs as co-solvents, or additives in various reaction systems, the recovery of ILs for recycle is a key process. Recently, Lee et al. studied the clean recovery of [BMIM]FeCl₄ rich phase from its mixture with water by using a magnetic

field [17]. However, this method failed to separate homogeneous mixtures which accommodated up to ~20% (v/v) [BMIM]FeCl₄. Although the conventional evaporation method is available, it is laborious to evaporate over 80 v% H₂O. In review of these, there is a need to develop a new methodology for recovery of [BMIM]FeCl₄ from homogeneous mixtures.

Here, we report a simple chemical method that can successfully separate [BMIM]FeCl₄ from the homogenous solution even with a low content of 1 v%. Extra evaporation method was used to remove the trace of H₂O in obtained [BMIM]FeCl₄.

EXPERIMENTAL

[BMIM][FeCl₄] was synthesized referring to Hamaguchi et al. [3]. In brief, equimolar FeCl₃·6H₂O and [BMIM]Cl were mixed with vigorous stirring. Several minutes later, dark brown [BMIM]FeCl₄ was formed, and the mixture was still stirred for 24 h. When the upper layer water was separated, the [BMIM]FeCl₄ was treated in vacuum oven at 60 °C for 48 h in order to remove trace H₂O dissolved in [BMIM]FeCl₄.

Mixtures of [BMIM]FeCl₄ and water with three volume ratios, 10 : 90, 5 : 95, and 1 : 99, were prepared and divided into two groups, Group-I and Group-II, according to the preparation methods. In Group-I, [BMIM]FeCl₄ was carefully added into H₂O without agitation, while in Group-II, [BMIM]FeCl₄ was added into H₂O with vigorous stirring in order to form a homogeneous mixture.

A recovery experiment was carried out in two steps: (1) Inorganic salts were added in the homogeneous mixture of [BMIM]FeCl₄ and H₂O, and then the mixture was vigorously agitated for 5 minutes. Subsequently, droplets of [BMIM]FeCl₄ appeared and were absorbed on the vessel walls. Unsaturated, saturated and overmuch saturated inorganic salts were added, respectively, in order to investigate the effect of concentration of inorganic salts on the recovery properties. (2) Immiscible mixture of [BMIM]FeCl₄ and H₂O was centrifuged at high-speed, or irradiated in an intensive magnetic field (max. 12 T); alternatively, organic solvents of CCl₄ or CHCl₃ were added in the immiscible mixture of [BMIM]FeCl₄ and H₂O, in order to aggre-

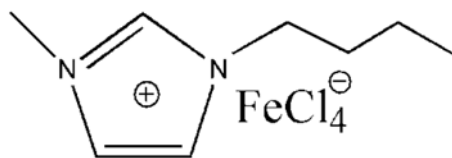


Fig. 1. Molecular structure of 1-butyl-3-methylimidazolium tetrachloroferrate, [BMIM]FeCl₄.

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gate the droplets of [BMIM]FeCl₄ to form a continuous phase layer under H₂O layer. CCl₄ or CHCl₃ not less than half of the mixture volume was added so as to entirely remove droplets of [BMIM]FeCl₄.

RESULTS AND DISCUSSION

In our primary experiment, magnetic response and recovery behavior of sample mixture solutions in Group-I and Group-II were tested in an ultrastrong magnetic field. For all Group-II samples in ultrastrong magnetic field (10 T) up to 10 v% for 15 minutes, no [BMIM]FeCl₄ was separated, while for Group-I samples, a distinctly magnetic response was observed even for those with lower content of [BMIM]FeCl₄ up to 5%. These indicate that the recovery of [BMIM]FeCl₄ depends on not only the volume ratio, but also the homogeneity of the mixture. Therefore, the first step of recovering [BMIM]FeCl₄ from aqueous solution is to divide the homogeneous solution of [BMIM]FeCl₄ and H₂O into two-phase.

Due to the hydrophobic property of [BMIM]FeCl₄ [8,14], the homogeneous mixture of [BMIM]FeCl₄ and H₂O may be an emulsion rather than a true solution. Therefore, a demulsification method can be used to separate [BMIM]FeCl₄ from H₂O. However, there is no distinct change that was observed by using ultracentrifugation at a high-speed of 60,000 rpm over 0.5 h or cryothermal treatment at a lower temperature (−18 °C) for 24 h.

Alternatively, the demicelle method by adding inorganic salts has a distinct effect on the separation of [BMIM]FeCl₄ from its aqueous mixture. Fig. 2 shows the photos of the homogeneous mixture of [BMIM]FeCl₄ (5 v%) and H₂O (95 v%) with and without the addition of saturated NaCl and/or CCl₄. It is clearly observed that the original mixture exists in the form of a transparent homogeneous orange liquid (Fig. 2(a)). For the mixture containing saturated NaCl, brown droplets appear and absorb on the vessel wall and bottom (Fig. 2(b)). Because the density of [BMIM]FeCl₄ (1.38 g/cm³) [6] is larger than that of H₂O (1.0 g/cm³), most of [BMIM]FeCl₄ gradually slid from vessel wall and launched on the bottom. With the further addition of organic solvents CHCl₃ (or CCl₄) a three-layer mixture forms (Fig. 2(c)), which is in the form of H₂O/[BMIM]FeCl₄/CCl₄ from up to down, consistent with the order of their densities: (H₂O: 1 g/cm³, [BMIM]FeCl₄: 1.38 g/cm³ [6], CHCl₃: 1.45 g/cm³). It is worth mentioning that the CHCl₃ or CCl₄ in the three-layer mixture can be reused without further treatment.

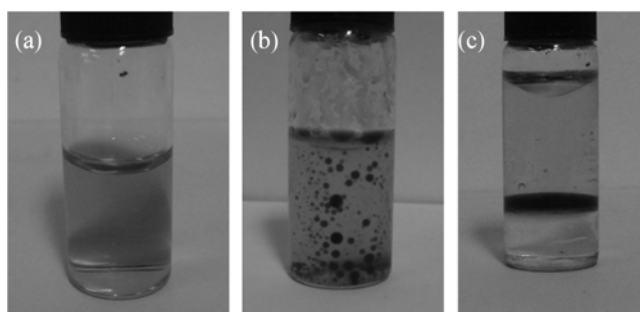


Fig. 2. Photos of homogeneous mixture of [BMIM]FeCl₄ (10 v%) and H₂O (90 v%) before (a), and after adding saturated NaCl (b), and further adding CCl₄ (c).

When the sample mixtures in Fig. 2(b) were further treated by ultracentrifugation method at a speed over 10,000 rpm or ultrastrong magnetic field, [BMIM]FeCl₄ was also successfully separated and formed a continuous phase layer, i.e., a two-layer mixture, H₂O/[BMIM]FeCl₄.

Furthermore, for those homogeneous mixtures with 5 v% [BMIM]FeCl₄ or more, when they were added with NaCl and vigorously agitated, bigger droplets of [BMIM]FeCl₄ appeared. Therefore, when the vessel (flat bottom) was tilted at some angle and rapped slightly, these big droplets of [BMIM]FeCl₄ moved and formed a continuous [BMIM]FeCl₄ phase. This fact suggests a much easier separation process without extra strong external force. However, with the help of ultracentrifugation and/or ultrastrong magnetic field, or chemical reagents, small [BMIM]FeCl₄ droplets as well as those adsorbing on the vessel wall and bottom could be entirely collected in a shorter time. In other words, the separation efficiency was improved by the presence of a strong external force.

Several other inorganic salts including KCl, CuCl₂, NaNO₃, Na₂SO₄ were used to separate [BMIM]FeCl₄ for comparison with NaCl, and the results are summarized in Table 1. It is concluded that the applied inorganic salts can be divided into three groups according to their separation performance: Na₂SO₄ and NaNO₃ show little effect, while KCl, CuCl₂ favor separation for those samples with higher volume ratio of [BMIM]FeCl₄ to H₂O, e.g., more than 5%. Only NaCl offers an excellent separation effect which can separate [BMIM]FeCl₄ from the homogeneous mixture even with only 1 v% [BMIM]FeCl₄. Recently, Rebelo et al. reported the biphasic effect of K₃PO₄ on [BMIM]Cl [18], which is not valid for [BMIM]FeCl₄. Since the inorganic salts dissolved poorly in [BMIM]FeCl₄ but well in H₂O, the inorganic salts can be easily regained from H₂O, e.g., via evaporation under sunshine.

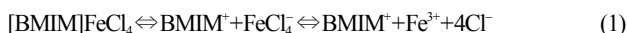
It is also found that the separation of [BMIM]FeCl₄ strongly depends on the concentration of inorganic salts in mixture of [BMIM]FeCl₄ and H₂O. Unsaturated NaCl caused little [BMIM]FeCl₄ droplet formation, while saturated NaCl promoted a much faster and more efficient separation process. However, when overmuch saturated NaCl was added, the separation process was hindered due to the adsorption of some [BMIM]FeCl₄ onto the undissolved NaCl particles.

As we know, dissolution of solutes in solvents depends on not only the temperature and its dissolution ability, but also the existence of other solutes: the dissolution increases or decreases when other solutes are added. Here, both inorganic salts are solutes, hence the dissolution of [BMIM]FeCl₄ was influenced by different inorganic salts and concentrations. When the dissolution of [BMIM]FeCl₄ decreased, it separated and recovered from the mixture. As shown in Table 1, this effect is selectively sensitive to anions: Only

Table 1. Phase-dividing performance of various inorganic salts to homogeneous mixture of [BMIM]FeCl₄ and H₂O

Volume ratio	10%	5%	1%
NaCl	good	good	mid
KCl	good	mid	/
CuCl ₂	good	mid	/
NaNO ₃	mid	mid	/
Na ₂ SO ₄	/	/	/

when those salts including anion Cl⁻ were added could a recovery process occur, while the other three anions, NO₃⁻, SO₄²⁻, PO₄³⁻ did not work. In other words, the addition of Cl⁻ anion favors the backward direction of the equilibrium in Eq. (1). On the other hand, the dissolution (recovery) also depends to some extent on cations, for different recovery performance was also found for NaCl, KCl and CuCl₂. The relevant mechanism needs further investigation.



The mutual solubility includes the solubility of the water in the IL-rich phase and the solubility of the IL in the water-rich phase [19]. Results of a primary experiment on the solution of [BMIM]FeCl₄ in H₂O and H₂O in [BMIM]FeCl₄ show that up to 20 v% [BMIM]FeCl₄ could be dissolved in 80 v% H₂O, while it is hard even for a spot of H₂O to be dissolved in pure [BMIM]FeCl₄ of much higher volume, e.g., 50 μL H₂O to 800 μL [BMIM]FeCl₄. Hence, the hydrophobic property of [BMIM]FeCl₄ refers to the solubility of H₂O in [BMIM]FeCl₄ rather than otherwise. This also indicates a trace of H₂O existing in the [BMIM]FeCl₄, which can be easily removed by evaporation method.

CONCLUSION

We present an easy recovery method for [BMIM]FeCl₄ from the homogeneous mixture even with a low content to 1%. Meanwhile, the inorganic salts and organic solvents used in the separating process can be recycled; thus, it is an efficient and low-cost method. Together with the way for immiscible [BMIM]FeCl₄-rich mixture, an overall means is available that can recover [BMIM]FeCl₄ from a mixture of [BMIM]FeCl₄ and H₂O with any volume ratio of [BMIM]FeCl₄ (1% ≤ C₀ < 100%).

ACKNOWLEDGEMENT

We are grateful for the support of the National Natural Science Foundation of China (No. 20504026, 20604015), International Scientific and Technological Cooperation Program of Shanghai (No. 08230705600), and Shanghai Nanotechnology Promotion Center (No. 0852nm02300), Shanghai Leading Academic Discipline Project

(B502) and Shanghai Key Laboratory Project (08DZ2230500).

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