Magnetic behavior of mixture of magnetic ionic liquid [bmim]FeCl₄ and water

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The magnetic response of the mixture of 1-butyl-3-methylimidazolium tetrachloroferrate ([bmim]FeCl₄) and water was investigated. The [bmim]FeCl₄ rich phase in the mixture forming two phases was easily separated under an external magnetic field. The homogeneous mixtures of [bmim]FeCl₄ and water were also attracted to the direction of the magnetic field. Under a gradually varied magnetic field, the concentration of the mixture varied as a function of the magnetic field strength. We confirmed the possibility of a magnetic recovery system using the mixtures of [bmim]FeCl₄ and water. © 2007 American Institute of Physics. [DOI: 10.1063/1.2710462]

I. INTRODUCTION

Room temperature ionic liquids (ILs) have gained wide popularity in recent years as extraction solvents, cosolvents, and media for catalytic reactions. ILs are merely liquids that are comprised entirely of ions. The main characteristics of ILs distinguished from classical molten salts are their low melting points. ILs are generally liquid at room temperature and can be used as reaction media. The interest for ILs stems from their potential as “green solvents” because of their non-volatile character and thermal stability. ILs are also able to dissolve many compounds such as polar and nonpolar organic, inorganic, and polymeric compounds. The physicochemical properties of ILs can be modified for the nature of the desired reactions by altering their cations and anions. This possibility for synthetic variation has led ILs to be described as Designer Solvents. ILs have been used as recyclable alternatives to organic solvents in organometallic reactions, in biocatalysis, for catalytic cracking of polyethylene, and for radical polymerization.

When ILs are used as extraction solvents for liquid-liquid separation and additives for azeotrope breaking and liquid chromatography, the key process is the recovery of ILs for the next cycle. Evaporation is one of the possible processes for the recovery of ILs. However, it takes too much energy to evaporate water or organic solvents and causes other environmental problems. Only a small amount of research on the reuse of ILs has been reported so far. Wong et al. used nanofiltration to reuse ILs after Suzuki reactions in the mixture of organic solvent and ILs.

Recently, magnetic behavior of 1-butyl-3-methylimidazolium tetrachloroferrate ([bmim]FeCl₄) defined as magnetic IL (MIL) was discovered. Several MILs containing Fe³⁺ which may also show magnetic behavior have been reported and the change of cation structure can alter the physicochemical properties of MILs. Because MILs have both general properties of ILs and strong magnetic response, a recovery system with MILs using a magnetic field has a great advantage regarding energy efficiency and simplicity. In this study, we investigated the possibility of phase separation of MILs for a magnetic recovery system.

II. PREPARATION OF MAGNETIC IL

The preparation of [bmim]FeCl₄ was carried out using similar method previously reported. By mixing commercially available solid [bmim]Cl (from C-TRI, Korea) and FeCl₃·6H₂O (from Sigma) with equimolar amounts, a dark brown liquid was obtained. The hydrophobic IL was purified by repeated washing with de-ionized water and evaporation. To measure the solubility of [bmim]FeCl₄ in water, 1 ml of both water and [bmim]FeCl₄ in a vial were vigorously mixed in a shaking incubator for 24 h at 25 °C. The phases were separated by centrifugation. The content of [bmim]FeCl₄ in the supernatant was determined by UV-visible spectroscopy (Genesys™ 5, Spectronic) at 210 nm, because the imidazolium ring present in the dialkylimidazolium based ILs absorbs strongly at this wavelength.


III. RESPONSE OF MIXTURES OF WATER AND MIL TO THE MAGNETIC FIELD

Since the ILs usually exist as mixtures with solvents when ILs are used as extraction solvents or additives, the magnetic behavior of a mixture of [bmim]FeCl₄ with water must be studied. The 20% (v/v) of [bmim]FeCl₄ was fully miscible with water after vigorously shaking, while a 50% mixture of water and [bmim]FeCl₄ formed two phases. In order to observe the response of the mixture to the magnetic field, the mixtures of water and [bmim]FeCl₄ with 5:5, 8:2, and 9:1 v/v ratios were placed between two electromagnet poles, respectively. Figure 1 shows the responses of the mixtures to the external magnetic field of 1 T. The [bmim]FeCl₄ rich phase in 50% mixture was attracted and moved toward the electromagnet pole, and the surface was concave. It means that a mixture of water and [bmim]FeCl₄ forming two phases can be successfully separated by a strong magnetic field of 1 T. Even though the surface shape was still concave, the phase separation of the fully miscible mixtures (<20%) was not clearly observed by naked eye with the magnetic field of 1 T.

For a more comprehensive analysis of the concentration variation of the mixture, a rectangular acryl chamber (2 × 11 × 3 cm³, thickness of 0.5 cm) containing the mixture was placed in the monopole electromagnet, as shown in the Fig. 2(a). The magnetic field gradually decreased as a function of the distance from the end of the pole. Samples were taken at every 1 cm interval from the pole. The concentrations of both [bmim]FeCl₄ and dissociated [bmim]⁺ in each sample were analyzed by UV-visible spectroscopy which detects the imidazolium ring on the cation (whether dissociated or undissociated). As the [bmim]⁺ dissociated from [bmim]FeCl₄ in water cannot be attracted to the electromagnet, the magnetic behavior of undissociated [bmim]FeCl₄ can be investigated from the concentration change of the imidazolium ring. It was shown that the concentration of [bmim]⁺ and [bmim]FeCl₄ decreased linearly as a function of the distance from the pole or the magnetic field strength in Fig. 2(b). The region closer to the electromagnet pole had a higher concentration, and the region farther from the pole had a lower concentration. Furthermore, the spatial average concentration was the same with the concentration of the mixture before applying the magnetic field. It implied that undissociated [bmim]FeCl₄ moved to the pole direction due to the attractive force from the pole. This is evidence of the possibility of phase separation using a magnetic field. From this result, the phase separation is expected to occur around the solubility of the [bmim]FeCl₄ (22.2% in water at 25 °C) within a moderate magnetic field. This investigation yielded very promising results for the magnetic recovery system application. The rate of concentration changes according to the magnetic field gradient, ∆C/∆H ~ 0.2% /T, obtained from the linear proximity. Because a commercially available superconducting magnet can generate a magnetic field of 7 T, technically ∆C = 1.4% of concentration difference is achievable by the magnetic field only. Even for the wide range of concentrations, phase separation will be possible using a strong magnetic field. On the other hand, several ILs containing Fe³⁺ which may also show magnetic behavior are already well known and it is expected that MILs which possess high magnetic susceptibility in water can be synthesized by changing the cation and anion structures.

The magnetic phase information of MILs is also important, but the phase of [bmim]FeCl₄ is liquid. It is not easy to measure the magnetic properties of the liquid with conventional tools; we employed the Faraday effect which is the rotation of the plane of linearly polarized light in a magnetic substance. The Faraday angle is given by \( \theta_F = V H d \), where \( V \), \( H \), and \( d \) are Verdet constant, a magnetic field, and propagation length, respectively. \( V d = \theta_F / H \) was determined from the linear hysteresis loops for the various concentrations of the mixtures, which are depicted in the Fig. 3. Monotonic decrement of the \( \theta_F / H \) with increasing concentration indicates that the \( V \) of MIL are negative because water is
a diamagnetic substance and $V_{\text{water}}$ is positive $[3.8 \times 10^{-6} \text{ rad/(G cm)}]$. Furthermore, the order of magnitude of $V_{\text{MIL}}$ is the same as the water. The magnetic moment of MIL is $4.06 \times 10^{-5} \text{ emu/g}$, which is $10^{-6}$ of the usual ferromagnetic materials. Above three experimental observations, linear hysteresis without saturation, small magnetic moment, and small $V$ values indicates that the [bmim]FeCl₄ is a paramagnetic substance, even though it is attracted by the magnetic field and phase separation is possible.

IV. CONCLUSIONS

We found that the [bmim]FeCl₄ rich phase in mixtures of [bmim]FeCl₄ and water forming two phases could be easily separated by a magnetic field, while the separation of only [bmim]FeCl₄ from a homogeneous mixture was not found while observing the magnetic field of 1 T. With more careful quantitative analysis, however, the concentration was spatially varied under the gradually decreased magnetic field. The phase separation is expected to occur around the solubility of the [bmim]FeCl₄ with a moderate magnetic field. In addition, the coupling of magnetic field and several conventional methods including filtration, ultracentrifugation, adsorption, and ion exchange chromatography can be used to recover dissociated compounds of MILs and increase the efficiency of recovery. Therefore, the use of magnet to recover MILs from reaction mixtures will be very useful and have great potential.

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