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SHORT COMMUNICATION

Recovery of magnetic ionic liquid [bmim]$FeCl_4$ using electromagnet

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Abstract−Recovery of 1-butyl-3-methylimidazolium tetrachloroferrate ([bmim]$FeCl_4$) from its mixture with water was investigated. The [bmim]$FeCl_4$ rich phase in the mixture forming two-phase was successfully separated, while homogeneous mixtures could not be separated. However, the concentration of the homogeneous mixture varied as a function of the magnetic field strength. Therefore, a combination of magnetic field and conventional methods to recover magnetic ILs from reaction mixtures will be very useful and have great potential.

Key words: Magnetic Ionic Liquid, Magnetic Behavior, Electromagnet, Reuse, Separation

INTRODUCTION

Room temperature ionic liquids (ILs) are organic salts that do not crystallize at room temperature [1]. The interest in ILs stems from their potential as ‘green solvents’ because of their non-volatile character and thermal stability, which makes them potentially attractive alternatives for volatile organic solvents [2]. ILs have been used for liquid-liquid extraction processes, as recyclable alternatives to aprotic solvents in organometallic reactions, in biocatalysis, for catalytic cracking of polyethylene and for radical polymerization [3].

When the ILs are used as cosolvents or additives in various reaction systems, the key process is the recovery of ILs for the next cycle. Evaporation is one of the possible processes for the recovery of ILs, but it takes too much energy to evaporate water and organic solvents or cause another environmental problem. Few researches on the reuse of ILs have been reported so far. Livingston et al. used the organic solvent nanofiltration to reuse ILs after Suzuki reactions in the mixture of organic solvent and ILs [4].

Recently, a magnetic IL, which shows a strong response to magnetic field, has been discovered [5]. Because 1-butyl-3-methylimidazolium tetrachloroferrate ([bmim]$FeCl_4$) has both general properties of ILs and strong magnetic response, the recovery system of this IL by using a magnetic field may be very easy and does not use high energy. In this study, we investigated the possibility of the use of a magnet to recover ILs after the ILs were used in a reaction system.

MATERIALS AND METHODS

The preparation of [bmim]$FeCl_4$ was carried out with a similar method previously reported [5]. By mixing commercially available solid [bmim]Cl (from C-TRI, Korea) and $FeCl_3 \cdot 6H_2O$ (from Sigma, USA) with equimolar amount, dark brown liquid was obtained. The hydrophobic IL was purified by repeated washing with deionized water and evaporation. In order to observe the response of magnetic IL to the magnetic field, we placed the magnetic IL between two poles of the electromagnet and applied a magnetic field of 0.5, 1, and 1.5 T. While the field was applied, only qualitative eye observation was performed by taking photographs. More quantitative experiments will be published elsewhere.

RESULTS AND DISCUSSION

We used an electromagnet which can change the strength of magnetic field to see the magnetic behavior of pure [bmim]$FeCl_4$, because it is difficult to see the response of magnetic IL with an NdFeB permanent magnet. By increasing the magnetic field, strong response change to the external magnetic field was observed.

Fig. 1 shows the response to the external magnetic field of pure [bmim]$FeCl_4$ with increasing magnetic field. The pure [bmim]$FeCl_4$ was strongly attracted by 1 T of magnetic field and its surface was changed to be concave upward. Hayashi and Hamaguchi showed that the shape of two layers containing [bmim]$FeCl_4$ and water was highly distorted with 0.55 T NdFeB permanent magnet [6]. However, it was observed in our experiment that at least 1 T is needed to see the magnetic behavior of pure [Bmim][$FeCl_4$].

Fig. 2 shows the responses to the external magnetic field of the mixture of [bmim]$FeCl_4$ and water. The 20% (v/v) of [bmim]$FeCl_4$ was fully miscible with water after vigorous shaking and 50% mixture of [bmim]$FeCl_4$ and water formed 2-phase; then the surface of the mixture was initially flat. The [bmim]$FeCl_4$ rich phase in 50% mixture was attracted and moved toward the electromagnet and the surface of the mixture changed to be concave upward. It means that the mixture of [bmim]$FeCl_4$ and water forming 2-phase can be successfully separated by a strong magnetic field of 1 T. However, a homogeneous mixture which contains [bmim]$FeCl_4$ less than 20% could not be separated by a magnetic field of 1 T, but the surface shape was changed. With increasing [bmim]$FeCl_4$ content, the surface of the mixture was highly distorted. In addition, preliminary results about the concentration profile of the mixtures of water and [bmim]$FeCl_4$ in a magnetic field showed the possibility of phase separation. The near region from the electromagnet pole has higher concentration, and the far region has lower concentration.

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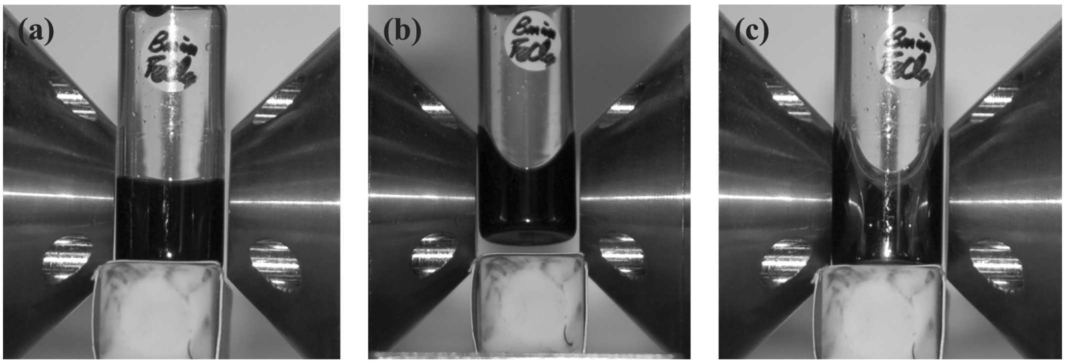

Fig. 1. The responses to the magnetic field of pure [bmim]$FeCl_4$. (a) 0.5 T, (b) 1.0 T, (c) 1.5 T.

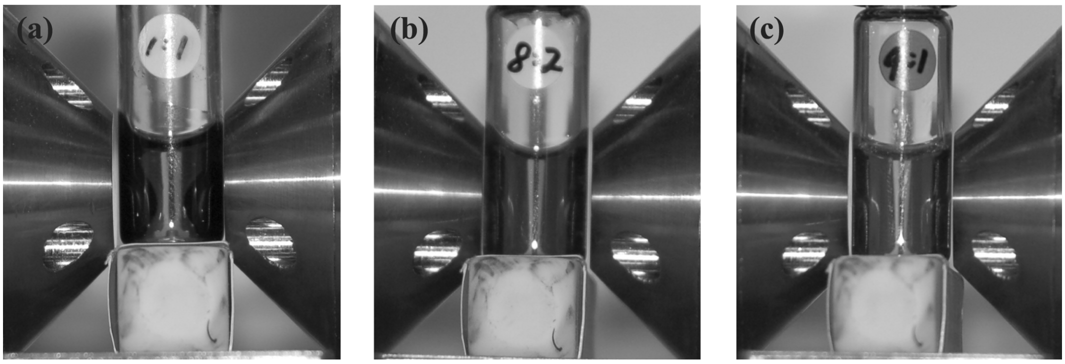

Fig. 2. The responses to the magnetic field (1 T) of a mixture of water and [bmim]$FeCl_4$. The volume ratio of water to [bmim]$FeCl_4$ is (a) 1 : 1, (b) 8 : 2, (c) 9 : 1.

Magnetic ILs not only have strong response to a magnetic field but also general properties of ILs including non-volatility and thermal stability. Therefore, they can be used as alternatives for organic solvents and separated by magnetic field after use in a reaction system. In this study, although the two phase mixture of [bmim]$FeCl_4$ and water could be easily separated by the magnetic field, the separation of only IL from a homogeneous mixture of IL and water could not be achieved at this time. It is thought that [bmim]$FeCl_4$ dissolved and dissociated in water may have too low magnetic susceptibility by the interference of water molecules. However, several ILs containing Fe^{3+} which may also show magnetic behavior are already known [7], and it is expected that magnetic ILs which possess high magnetic susceptibility in water can be synthesized by changing the cation and anion structure. For example, ILs containing 1-butyronitrile-3-methylimidazolium cation [6] were prepared and the mixtures of $FeCl_3$ and $FeCl_4$ were also used to synthesize [bmim] ILs [8]. On the other hand, the coupling of a magnetic field and several conventional methods including ultracentrifugation, filtration, and adsorption by using the properties of ILs such as high molecular weight, density, and conductivity may increase the efficiency of recovery. For example, locally increased concentration of magnetic ionic liquid can increase the efficiency of ultracentrifugation. Therefore, the use of a magnet to recover ILs from reaction mixtures will be very useful and have great potential.

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