

Extraction of magnetic nanoparticles using magnetic ionic liquids

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Magnetic nanoparticles display a range of unique properties of interest to fields such as water treatment, drug delivery, catalysis, and many more. Widespread use of magnetic nanoparticles relies heavily on one's ability to separate them effectively from other media, for example in water treatment. In this work, an efficient method to separate magnetic nanoparticles from organic solvent using magnetic ionic liquids is demonstrated for the first time. Fourier transform infrared spectroscopy, ultraviolet–visible spectroscopy, and microscopy were employed to investigate the authors' model system. This work will greatly impact future directions in the science of separating nanoparticles and applications of ionic liquids.

1. Introduction: Magnetic nanoparticles (MNPs) display a range of interesting properties, such as magnetism, finite-size effects, and surface effects [1]. These properties suggest a range of potential applications in fields such as water treatment [2], separation [3–7], magnetic fluids [8], catalysis [9], biomedicine [10], and drug delivery [11]. In conventional methods for recycling, MNPs are separated from solution by use of magnets or other external magnetic fields. However, in many instances, MNPs are difficult to separate from a solution using these techniques. For example, in the process of water treatment using MNPs, there is still uncertainty about whether MNPs are properly separable and the effectiveness of the process [12].

Ionic liquids (ILs) are environmentally friendly media and have many advantageous properties, such as (i) low vapour pressure; (ii) high thermal and chemical stability; (iii) excellent electrochemical properties; (iv) excellent solubility in both inorganic and organic chemicals; (v) switchable polarity and phase behaviour; (vi) low melting points. Many ILs remain in the liquid phase at temperatures as low as $-60\text{ }^{\circ}\text{C}$. This could be useful for applications of ILs in cold climates; (vii) functional groups of ILs can be designed to tailor desired properties. Due to this broad range of tunable physical and chemical properties, ILs are currently being utilised in many fields, such as CO_2 capture and storage [13, 14], catalysis [15–19], nanoscience [20–23], biotechnology [24], cellulose science [25], and others. Magnetic ILs not only have the above advantageous properties of ILs, but also are types of materials showing magnetic properties. Therefore, magnetic ILs have more advantages and potential application prospects than conventional solvents in catalytic reactions, solvent effects, and separation processes [26]. Hayashi and Hamaguchi reported the magnetic properties of 1-butyl-3-methylimidazolium tetrachloroferrate (BmimFeCl_4) for the first time in 2004 [27]. Magnetic ILs can be utilised in fluid–fluid separation process [27]. Magnetic extraction phases have been employed in nucleic acid analysis for rapid DNA extraction. In addition, magnetic ILs can enhance the extraction efficiency to extract DNA. It means that less volumes of the IL extraction solvent is needed for DNA extraction compared with the traditional extraction solvents [28].

There is some research on utilising both ILs and nanotechnology, for example, in catalytic processes [29] and to use ILs to modify the surface of nanoparticles [30]. However, to our knowledge, there are no reports on the utilisation of magnetic ILs as solvents to extract MNPs from solutions. In this Letter, we report the use of a magnetic IL as a medium for extraction of MNPs from an organic solvent.

The magnetic IL BmimFeCl_4 and Fe_3O_4 MNPs have been studied in this Letter.

In the conventional methods, MNPs are separated from solutions for recycling by using magnets or another external magnetic field. We have found that Fe_3O_4 MNPs cannot be separated efficiently from toluene using these methods. However, if a magnetic IL such as BmimFeCl_4 is interfaced with the sample of Fe_3O_4 MNPs in toluene, it can be shown that this enhances the extraction of the nanoparticles from the organic solvent. This occurs without the use of magnets or other external magnetic fields. Presumably, the strong interactions between Fe_3O_4 MNPs and BmimFeCl_4 lead to effective extraction of Fe_3O_4 MNPs from toluene.

2. Experiments: Both BmimFeCl_4 and Fe_3O_4 MNPs display magnetic behaviours. BmimFeCl_4 was synthesised in our laboratory according to the reaction scheme shown in Fig 1. BmimFeCl_4 was characterised using Fourier transform infrared. In addition, Fig 2 showed that our in-house prepared IL BmimFeCl_4 displayed magnetic properties in the presence of magnets.

Commercially available MNPs come in a toluene solution and, as such, we have demonstrated our concept on extraction of MNPs from this solvent. Fe_3O_4 MNPs in toluene solution was purchased from Sigma-Aldrich Co. (5 mg/ml; average MNPs size: 10 nm). This solution was diluted with toluene to obtain a sample of 0.035 wt% concentration (SA). Subsequently, SA was divided into two equal parts and BmimFeCl_4 was added to one of them to obtain sample SB. The resulting solution SB has a mass ratio of BmimFeCl_4 : Fe_3O_4 MNPs: toluene of 27.5: 1.8: 5290. In conventional methods, a magnet or magnetic field would be applied to separate MNPs from solutions. Therefore, magnets were also utilised herein to separate Fe_3O_4 MNPs from toluene in sample SA for comparison.

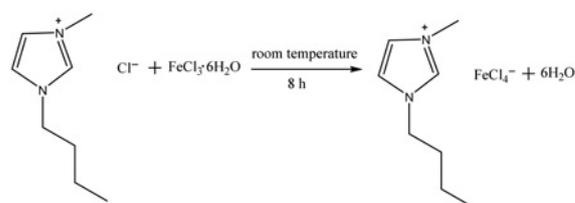


Fig. 1 Chemical reaction to obtain magnetic IL BmimFeCl_4

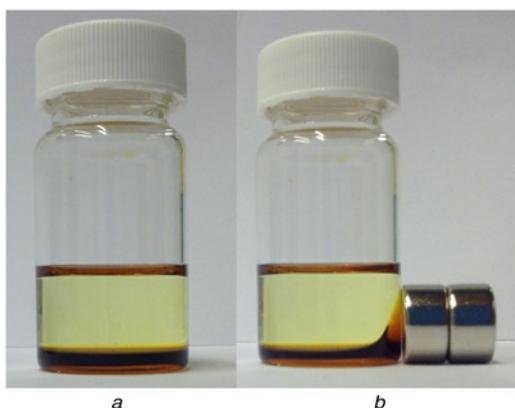


Fig. 2 Magnetic properties of $BmimFeCl_4$ (lower phase: $BmimFeCl_4$; upper phase: toluene)
a Without external magnetic field
b With external magnetic field

3. Results and discussions: The magnetic IL $BmimFeCl_4$ does not disperse in toluene. In sample SB (left), there are two liquid phases: the toluene phase (upper) and IL phase (lower). The Fe_3O_4 MNPs are predominantly in the toluene layer, which leads to the reddish brown colour of this phase. In addition, the colour of the toluene phase of SA (right) and SB is similar, suggesting similar concentrations of MNPs in SA and SB.

The fresh samples of SA and SB were shown in Fig. 3*a*. Samples SA and SB were kept quiescently under an external magnetic field for 2 days (Fig. 3*b*). In both samples, optically large-sized MNPs were concentrated at the bottom of the sample due to the effect of the external magnetic field. However, the concentration of MNPs in SA is still high and the MNPs in SA can be easily dispersed into the toluene solution upon shaking.

Subsequently, samples SA and SB were shaken by hand and kept quiescently for various times. After only 3 min, the concentration of Fe_3O_4 MNPs in the toluene phase of SB decreased significantly (Fig. 3*c*). This shows that the MNPs rapidly migrate into the magnetic IL phase. After 4 h (Fig. 3*d*), the toluene phase is transparent. The concentration of Fe_3O_4 MNPs in the toluene phase of SB is low, while most of the MNPs reside in the IL phase. After 2 days (Fig. 3*e*), the toluene phase was even more transparent, suggesting that the concentration of MNPs was further decreased. The Fe_3O_4 MNPs appear to strongly favour residing in the IL phase, and they can further be easily separated using magnets and filtration.

To demonstrate that the separation occurs without any contact between the sample and external magnetic fields, further extraction experiments were conducted. Fig. 4*a* shows freshly prepared samples of SB (left) and SA (right) kept quiescently for 19 h without prior exposure to magnetic fields. The toluene phases are similar and indicate the presence of MNPs. Subsequently, the samples were shaken by hand and kept quiescently for 3 min (Fig. 4*b*). No separation occurred in sample SA, whereas a clear decrease in MNP concentration was observed in the toluene phase of sample SB. After another 4 h undisturbed, sample SB (Fig. 4*c*) clearly demonstrates the further decrease of MNPs in the toluene phase. These experiments confirm that the separation process effectively occurs without the external magnetic influence.

The samples in Fig. 3*e* were further analysed by ultraviolet–visible (UV–Vis) spectrometry to demonstrate quantitatively the differences in MNP content of the toluene phases (Fig. 5). The high MNP content in sample SA is clear from the blue line showing relatively large and increasing absorbance towards lower wavelengths – indicating a large amount of MNPs present. In comparison, the toluene phase of SB (green line) shows absorption characteristics that demonstrate a very low MNP concentration. The 424-fold diluted sample of SA (red line) and the 2120-fold

diluted sample of SA (purple line) display virtually identical absorption characteristics to that of the toluene layer of SB, which further supports these conclusions. When compared with the

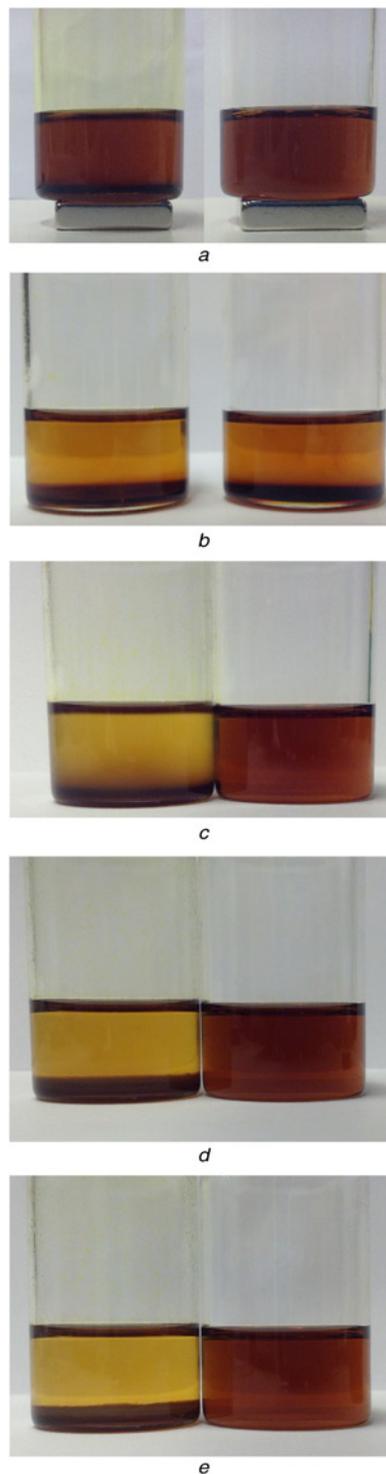


Fig. 3 Phase behaviour of SA (right) and SB (left)
a Fresh samples
b Samples kept quiescently in the presence of an external magnetic field for 2 days
c Samples kept quiescently for 3 min after shaken by hand without an external magnetic field
d Samples kept quiescently for 4 h after shaken by hand without an external magnetic field
e Samples kept quiescently for 2 days after shaken by hand without an external magnetic field

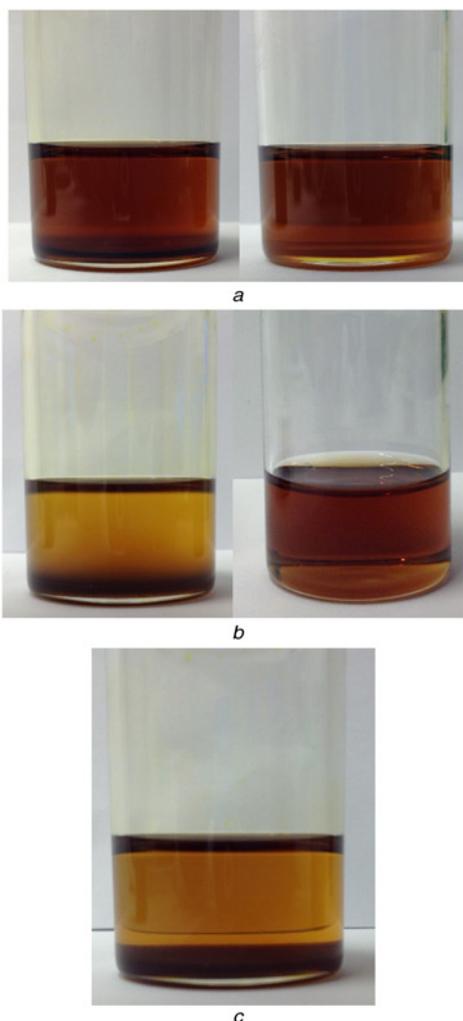


Fig. 4 Phase behaviour of SA (right) and SB (left) in the absence of magnetic field

- a Fresh sample kept quiescently for 19 h
 b Samples kept quiescently for 3 min after shaken by hand
 c Sample SB kept quiescently for 4 h after shaken by hand

spectrum of pure toluene (black line), it is clear that the SB toluene phase contains a comparatively small amount of MNPs.

Finally, microscopy was used to study the aggregated MNPs in the different phases (Fig. 6). It was observed that large-size aggregated MNPs are formed in the lower phase of SB and that no visible MNPs were demonstrably present in SA and the toluene phase of

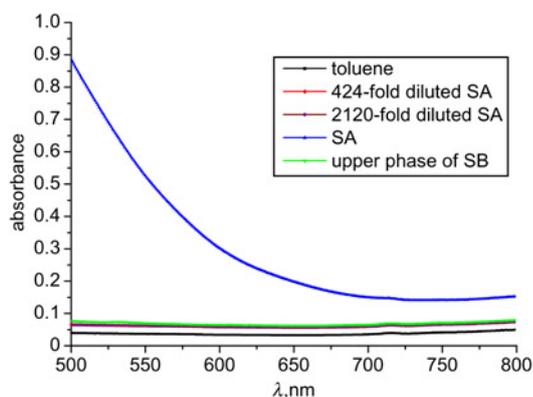


Fig. 5 UV-Vis curves of samples



Fig. 6 Micrographs (100 times) of SA (left), the upper phase of SB (middle), and the lower phase of SB (right)

SB. These results clearly demonstrate that MNPs are effectively extracted from toluene into the IL phase.

4. Conclusions: In conventional approaches, magnets or other external magnetic fields are utilised to separate MNPs from solutions. In this Letter, we have found that Fe_3O_4 MNPs can be separated efficiently from toluene using the magnetic IL BmimFeCl₄ in the absence of an external magnetic field. This demonstrates that BmimFeCl₄ magnetic IL can be utilised for Fe_3O_4 MNPs separation from toluene. This is a new method for efficient separation of Fe_3O_4 MNPs from toluene. Magnetic ILs are promising solvents for high-efficiency extraction of MNPs and further studies are currently underway in our laboratories to study the general applications of this approach.

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6 References

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