Cooperative intramolecular interaction of diazacrown ether bearing β-diketone fragments on an ionic liquid extraction system[†]

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A novel extractant β -diketone-substituted diaza-18-crown-6 demonstrated very efficient extraction of Sr²⁺ due to an intramolecular synergistic effect on the ionic liquid extraction system and recovery of Sr²⁺ from the ionic liquid was successfully achieved under acidic conditions.

Ionic liquids (ILs) have recently received growing attention as a new class of solvents. ILs, which are composed of an organic cation and either an organic or an inorganic anion, have different properties from those of molecular liquids.¹ Not only are ILs environmentally more attractive than organic solvents, but they possess tunable solvent properties such as polarity, hydrophobicity and solvent miscibility. These solvent properties are dependent on the combination of cations and anions. For example, ILs can be made hydrophobic while retaining ionicity. This dual nature has led to their use as novel extracting media for the solvent extraction of ionic species.²

Solvent extraction is one of the most effective analytical methods for the separation and purification of target substances. Currently, IL-based extraction systems of a variety of substances (e.g. metal ions,³ organic compounds⁴ and proteins⁵) have been widely investigated. In comparison to organic solvents, ILs show remarkably high performance for the extraction of strontium ions (Sr^{2+}) when using crown ethers as the extractant.⁶ Furthermore, the extraction mechanism changes from an ion pair extraction in organic solvent systems to a cation-exchange extraction process, in which Sr²⁺ is exchanged for the cationic constituent of the ILs.⁷ (Specifically, the predominant partitioning mode is dependent on the hydrophobicity of the ILs.⁸) However, this system has difficulty in the back extraction of the extracted metal ions because this system provides high extraction performance which is independent of the acid and salt concentrations in the aqueous phases. A similar phenomenon is also observed in extraction systems using other neutral extractants.^{3a,c} In contrast, anionic extractants enable back extraction of metal ions from ILs into acidic aqueous solutions. However, most anionic extractants, except β -diketone type ligands such as HTTA,⁹ show comparable extraction performance and a similar extraction mechanism between IL and organic solvent systems.¹⁰ More recently, synergistic extraction systems in ILs were achieved by the combination of crown ethers and other ligands.¹¹

We have been interested in the development of novel extractants suitable for IL-based extraction systems. The extractant plays a key role in the extraction efficiency and selectivity of metal ions. Unfortunately, there has been little progress in the development of novel extractants,12 and commercially available extractants are employed in most studies on IL-based extraction systems. In the present study, we have synthesized diaza-18-crown-6 bearing two 4-acyl-5-pyrazolones (H2BDA18C6) as a novel extractant for ILbased extraction systems (synthetic procedure in ESI[†]).¹³ 4-Acyl-5-pyrazolone derivatives are powerful β -diketone-type chelating reagents¹⁴ and are soluble in ILs. The compounds are expected to improve the extraction performance of diazacrown ethers in ILs. Furthermore, nitrogen atoms in a diazacrown ether may be capable of back extraction of metal ions.12,15 To assess the extraction performance of H2BDA18C6, the extraction behavior of Sr²⁺ using H2βDA18C6 into 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([C2mim][Tf2N]) was compared with those using 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (HPMBP), N,N'-dibenzyl-4,13-diaza-18-crown-6 (DBzDA18C6) and the mixture of HPMBP and DBzDA18C6. In addition, the differences in the extraction behavior between the IL and chloroform systems are discussed.[‡] The molecular structures of extractants and the IL employed in this study are shown in Fig. 1. We describe herein that H2BDA18C6 provides a remarkably high performance for Sr²⁺ extraction due to a cooperative "intramolecular" interaction when compared with the "intermolecular" synergy extraction system of the mixture of HPMBP and DBzDA18C6. The extraction performance of H2BDA18C6 is greatly enhanced



Fig. 1 Molecular structures and abbreviations of the ionic liquid and the extractants.

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by dissolution in the IL compared with in chloroform. The back extraction of Sr^{2+} from the IL into a receiving phase was successfully achieved under acidic conditions.

Fig. 2 shows the extraction behavior of Sr²⁺ in the chloroform (a) and IL (b) systems with H2BDA18C6 as a function of pH in the aqueous phase. The extraction behavior of these two systems was compared with those with other extractants. The concentration of DBzDA18C6 was equal to that of H2BDA18C6, but the concentration of HPMBP was two-fold greater than H2BDA18C6. This difference in concentrations was to ensure that the same number of functional β-diketone groups were available. In the chloroform system, neither HPMBP nor DBzDA18C6 were very effective at Sr²⁺ extraction. In contrast, when using the mixture of HPMBP and DBzDA18C6, the extraction of Sr²⁺ was significantly enhanced with increasing pH. These results clearly show that the combination of HPMBP and DBzDA18C6 generate a synergistic effect for Sr²⁺ extraction. HPMBP probably neutralizes the cationic charge of Sr²⁺ whereas DBzDA18C6 most likely replaces the hydration waters of Sr²⁺, thereby yielding a more organophilic metal complex. H2BDA18C6 provided a rather powerful extraction performance when compared with the mixture of HPMBP and DBzDA18C6, but was not able to transfer fully the Sr²⁺.



Fig. 2 Dependency of Sr^{2+} extraction on the aqueous phase pH in the chloroform system (a) and in the $[C_2mim][Tf_2N]$ system (b). Aqueous phase: $[Sr^{2+}] = 0.01$ mM. Extracting phase: [HPMBP] = 2 mM, [DBzDA18C6] = 1 mM and $[H2\beta DA18C6] = 1$ mM. The HPMBP system (black symbols), the DBzDA18C6 system (blue symbols), the HPMBP + DBzDA18C6 system (green symbols) and the H2 β DA18C6 system (red symbols).

Although the partitioning of Sr^{2+} using only HPMBP was negligible in the [C₂mim][Tf₂N] system, the extraction performance of DBzDA18C6 improved with increasing pH. This is contrary to the results in the chloroform system. Slope analysis as a function of the equilibrium pH (Fig. S1 in ESI†) showed that the slope of the logarithmic plots of the distribution ratio of Sr^{2+} versus pH was 1. This result suggests that one proton from protonated DBzDA18C6 (pK₁ = 7.5, pK₂ = 6.83)¹⁶ was released to extract the divalent cation Sr^{2+} . It is noteworthy that the number of released protons is not equivalent to the valence of Sr^{2+} . The transfer of Sr^{2+} with DBzDA18C6 into [C₂mim][Tf₂N] proceeds via the exchange reaction of Sr2+ for one proton and one C₂mim⁺. Consequently, this reaction maintains the charge balance during the partitioning process. Very similar extraction plots were obtained in the HPMBP and DBzDA18C6 mixed system when compared with those using only DBzDA18C6. We confirmed that the extraction dependence of Sr²⁺ on the HPMBP concentration in the mixed system was negligible. This result indicates that HPMBP cannot act as a synergistic reagent in [C₂mim][Tf₂N] because transfer of Sr²⁺ into [C₂mim][Tf₂N] was possible without neutralizing the cationic charge of Sr^{2+} by HPMBP. This observation contrasts with the results from the chloroform system. Probably, the extraction mechanism of Sr²⁺ in the system mixed with HPMBP and DBzDA18C6 is identical to that in the system with only DBzDA18C6 present. Interestingly, H2BDA18C6 enables the transfer of Sr²⁺ from the more acidic aqueous solutions compared with the system mixed with HPMBP and DBzDA18C, that is, H2βDA18C6 in [C₂mim][Tf₂N] possesses considerably high extraction performance for Sr²⁺. The covalent attachment of two β -diketone groups to a diazacrown ether leads to a dramatic increase of the extraction efficiency for Sr²⁺. Although the structure of the extracted species is not exactly known, it is justified to assume that the two β -diketone groups are in close neighborhood to Sr²⁺ bound by azacrown ether. In that sense, the dramatic increase of the extraction performance may be due to a kind of "intramolecular" synergistic effect.¹⁷ Furthermore, a slope analysis gave linear plots with a slope of 2, indicating that two protons from protonated H2BDA18C6 were released to extract Sr²⁺. Thus the transfer of Sr²⁺ with H2βDA18C6 into $[C_2 mim][Tf_2 N]$ proceeds via the proton exchange reaction.

To evaluate the difference in the extraction performance of H2 β DA18C6 for Sr²⁺ between [C₂mim][Tf₂N] and chloroform, the extractability of Sr²⁺ with increasing H2 β DA18C6 concentration in [C₂mim][Tf₂N] or in chloroform was compared (Fig. 3). This trial was performed under the same condition (pH 7.0) for the IL and chloroform systems. The extraction performance of H2 β DA18C6 for Sr²⁺ was significantly higher in [C₂mim][Tf₂N] than in chloroform. Only 0.1 mM of H2 β DA18C6 was required to quantitatively extract Sr²⁺ into [C₂mim][Tf₂N]. In the chloroform system, however, only modest extraction was observed at the same H2 β DA18C6 concentration. ILs can provide an appropriate environment that contributes to the performance of H2 β DA18C6. The reason why H2 β DA18C6 gives rise to a cooperative



Fig. 3 Dependency of Sr^{2+} extraction on H2 β DA18C6 concentration in chloroform (open symbols) and in [C₂mim][Tf₂N] (closed symbols). Aqueous phase: [Sr²⁺] = 0.01 mM, pH 7.0.

"intramolecular" interaction only in the IL-based extraction system is not fully understood and is currently under investigation.

Furthermore, the back extraction of Sr^{2+} extracted by H2 β DA18C6 in [C₂mim][Tf₂N] was performed under the pH control of the receiving phase. As shown in Fig. 4, the degree of back extraction of Sr^{2+} was enhanced as the acidity of the receiving phase was increased. This is because H2 β DA18C6 loses its coordination ability under acidic conditions. The extraction and recovery of Sr^{2+} using H2 β DA18C6 in the IL was readily switched by simply controlling the pH of the aqueous solutions.



Fig. 4 Back extraction of Sr^{2+} from $[C_2mim][Tf_2N]$. Aqueous phase: $[Sr^{2+}] = 0.01$ mM. Extracting phase: $[H2\beta DA18C6] = 1$ mM. Receiving phase: HEPES–HNO₃ or HEPES–LiOH solutions.

In conclusion, we have reported the first study on the "intramolecular" synergistic extraction of a metal ion in an ILbased system. The stripping of metal ions extracted in the IL was achieved under acidic conditions. The present findings suggest that modification of crown ethers with appropriate ligands can create considerable potential as novel extractants. In parallel with this study, we are investigating the extraction performance of H2 β DA18C6 for other metal ions in an effort to evaluate its application range. The development of novel synthetic receptors suitable for IL-based extraction systems is also currently under investigation.

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Notes and references

‡ Extracting phases were prepared by dissolving each extractant in $[C_2mim][Tf_2N]$. For comparison with the performance of IL, a conventional organic solvent, chloroform, containing each extractant was also prepared using the same procedures. Aqueous phases were prepared by dissolving 0.01 mM Sr(NO₃)₂. The pH of the aqueous solutions was

adjusted by the addition of HNO₃ or LiOH into HEPES buffer. Equal volumes of the extracting and aqueous solutions were mixed and shaken using a vortex mixer at 25 °C for 30 min to attain equilibrium. These mixtures were centrifuged for 3 min to promote phase separation. After phase separation, Sr²⁺ in the extracting phase was back-extracted into a HNO₃ solution (pH 2). The concentrations of Sr²⁺ in the aqueous phase and the receiving phase were determined using inductively coupled plasma mass spectrometry (ICP-MS, Hewlett Packard HP 4500) to obtain the extractability (= [Sr²⁺]_{ext}/[Sr²⁺]_{mi} × 100), the distribution ratio (= [Sr²⁺]_{ext}/[Sr²⁺]_{aq}) and the degree of back extraction (= [Sr²⁺]_{rec}/[Sr²⁺]_{ext}, the aqueous phase, the receiving phase and the initial condition, respectively. The equilibrium pH values in the aqueous phase were also measured.

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