Extraction of Rare-Earth Ions with an 8-Hydroxyquinoline Derivative in an Ionic Liquid

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The extraction behavior of rare-earth ions with an 8-hydroxyquinoline derivative, HO8Q (5-octyloxymethyl-8-quinolinol), was studied using an ionic liquid, [C₈mim][Tf₂N] (1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide), as the extracting phase. Compared with a conventional organic solvent, n-dodecane, the ionic liquid system showed a higher extraction ability for a heavy rare earth, Dy, and a better selectivity between Dy and Nd (separation factor $\beta_{\text{Dy/Nd}}$: 108). In the liquid-liquid extraction system, the color of the extracting phase changed from colorless to light yellow along with the extraction of rare-earth ions. Furthermore, the extraction efficiency was enhanced by the addition of TOPO (trin-octylphosphine oxide) as a co-extractant.

1. Introduction

Ionic liquids (ILs) have been highlighted as an alternative to conventional organic solvents in liquid-liquid extraction. The application of ILs to the extraction and separation of metal ions including rare-earth ions has been promoted by employing commercial extractants and some effective results have been obtained [1-4]. For example, the extraction performance of strontium and rare-earth ions with DC18C6 (dicyclohexano-18-crown-6) and CMPO (octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide), respectively [5,6], was significantly improved in an IL compared to that in conventional organic solvent, and the selectivity between individual ions was enhanced in the latter CMPO case. However, it was found that stripping was very difficult in the IL systems using such neutral extractants. In the IL systems employing proton dissociation type extractants such as D2EHPA (di(2-ethylhexyl)phosphoric acid) and PC-88A (2-ethylhexylphosphonic acid mono-2-ethylhexyl ester), the
Extraction performance was low due to their poor solubility, although stripping was possible [7,8].

One of the other commercial extractants 8-hydroxyquinoline (8-quinolinol) and its derivatives, which are known to have good extraction ability for various metal ions such as Cu(II), Zn(II), Mo(VI), Ga(III) and Hg(II), have been widely utilizing in analytical chemistry and hydrometallurgy [9-14]. Recently, 8-quinolinol derivatives have been applied to the extraction of rare-earth ions, and some interesting results have been reported in a conventional organic solvent system [15-17].

In the present work, an 8-hydroxyquinoline derivative, HO8Q (5-octyloxymethyl-8-quinolinol), was selected and applied in an IL-mediated liquid-liquid extraction system for rare-earth ions because HO8Q, which is a proton dissociation type extractant, is soluble in an IL [C₈mim][Tf₂N] (n = 8, 12). Extraction of three different rare-earth ions, Nd, Eu and Dy, which are important elements for technological devices, was investigated in the IL system and compared to that using a conventional organic solvent, n-dodecane. The extraction ability of 8-quinolinol derivatives for rare-earth ions are generally not so high, thus a synergistic system was examined using TBP (tributyl phosphate), TOPO (tri-n-octylphosphine oxide) and LIX63 (5,8-diethyl-7-hydroxydodecan-6-oxime) as co-extractants in the IL system.

2. Experimental

2.1. Reagents

The extractant HO8Q was purchased from Wako Pure Chemical Industries, Ltd. The ionic liquid [C₈mim][Tf₂N] (Lot: J00128.1, 99%) was supplied by Ionic Liquids Technologies GmbH Inc. TOPO and TBP were from Wako Pure Chemical Industries, Japan and LIX® 63 was provided by Henkel Corporation. The other chemicals were of reagent grade. The molecular structures and abbreviations for the extractants and the ionic liquid used in this study are shown in Figure 1.

![Molecular structures of extractants and the ionic liquid used in this study.](image)

2.2. Procedure

Extraction equilibria were measured by the conventional method. The feed aqueous phases containing 0.1 mM each of three rare-earth metal ions were prepared by dissolving their nitrate salts in
aqueous solutions containing 0.1M HNO₃ or 0.1M CH₃COONa. The pH values of the feed aqueous phases were adjusted by mixing these two solutions and/or by adding a drop of 1M NaOH solution. The extracting phases were prepared by dissolving 10mM HO8Q in an ionic liquid: [C₈mim][Tf₂N] or in n-dodecane, respectively. For the synergistic extraction systems, the extracting phases containing HO8Q and a co-extractant, 10 mM each, were prepared.

Equal volumes of the aqueous and IL phases were transferred to a sealed polypropylene test tube. The mixture was vigorously shaken by a vortex mixer for 10 minutes to attain equilibrium (298 K). The mixtures were centrifuged for 3 minutes (5000 rpm, 298 K) and the concentrations of the metal ions in the aqueous phases were determined with an ICP-atomic emission spectrometer (Perkin Elmer Co., Optima 5300) after phase separation. Then the extraction degree, $E$ [-], and the distribution ratio ($D$) were calculated by the following equations:

$$E = \frac{([M]_{aq,0} - [M]_{aq})}{[M]_{aq,0}}$$

$$D = \frac{([M]_{aq,0} - [M]_{aq})}{[M]_{aq}}$$

where $[M]$ represents the rare-earth ion concentration and the subscript $aq$ denotes the aqueous phase, and 0 is the initial state.

### 3. Results and Discussion

#### 3.1. Extraction of rare-earth ions with HO8Q

Figure 2 shows the extraction equilibrium of Nd, Eu and Dy with HO8Q in the IL and $n$-dodecane systems. Under the present conditions, the extraction degree of the metal ions increased with an increase in...
the pH values higher than 5.5. Therefore it was assumed that the extraction reaction proceeded via a proton-exchange mechanism. The resulting extracting lower or upper phases for the IL or the organic solvent system, respectively, turned from a colorless to a yellow solution with the progress of metal extraction. Thus the extraction of the rare-earth ions is also visible by the naked eye.

Figure 3 shows the relationship between log $D$ and pH for the extraction of rare-earth ions with HQ8Q in the IL or n-dodecane systems. HO8Q:10 mM, rare-earth ion: 0.1 mM.

Figure 3 shows the relationship between log $D$ and the equilibrium pH, and the linear relationship with slope 3 was obtained for each metal ion in the IL and n-dodecane systems. Here, it was found that the extractability of the heavy rare earth Dy in the IL system was higher than that in the n-dodecane system, however the extractability of the light rare earth, Nd, was lower than that in the n-dodecane system as shown in Figures 2 and 3. As for the middle rare earth, Eu, the extraction efficiency in both systems was similar. Similar behavior wherein the selectivity between light and heavy rare-earth ions was increased in the ILs compared to that in the organic solvent was observed for other extractants such as PC-88A and recently developed DODGAA ($N,N$-dioctyldiglycol amic acid) [8,18].

It has been reported that rare-earth ions are extracted with 3 molecules of 8-quinolinol (HR) in a conventional solvent extraction system as follows [17,19]:

$$M^{3+} + 3HR_{org} \rightleftharpoons MR_{3,org} + 3H^+ \quad (3)$$

More recently, it was shown that the extracted species for rare-earth ions with an 8-quinolinol derivative into an IL, 1-butyl-3-methyl-imidazolium hexafluorophosphate ($[C_4mim][PF_6]$) were $MR_3$ complexes [20]. Based on the results shown in Figure 3 and the previous reports described above, Eq. (3) was adopted as the extraction reaction in the present IL and organic solvent systems.

The extraction equilibrium constant $K_{ex}$ in Eq. (3) is defined in Eq. (4), and Eq. (4) can be converted to Eq.
(5) by using the distribution ratio $D$.

$$K_{\text{ex}} = \frac{[M]_{\text{org}}[H]^3}{[M]_{\text{aq}}[HR]^3_{\text{org}}} \quad (4)$$

$$\log D = \log K_{\text{ex}} + 3\log[H]\text{org} + 3pH \quad (5)$$

Based on Eq. (5), the values of $K_{\text{ex}}$ were calculated from the experimental data in Figure 3. The results are listed in Table 1 along with the separation factors ($\beta$).

Table 1. The values of $K_{\text{ex}}$ and separation factors ($\beta$)

<table>
<thead>
<tr>
<th></th>
<th>$K_{\text{ex}}$</th>
<th>$\beta$ (Kex1/Kex2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nd</td>
<td>Eu</td>
</tr>
<tr>
<td>n-Dodecane</td>
<td>$1.45 \times 10^{-15}$</td>
<td>$7.75 \times 10^{-15}$</td>
</tr>
<tr>
<td>[C8mim][Tf2]</td>
<td>$8.71 \times 10^{-16}$</td>
<td>$7.49 \times 10^{-15}$</td>
</tr>
</tbody>
</table>

As shown in Table 1, the separation factors for the three rare-earth ions, $\beta$ (Dy/Nd), $\beta$ (Dy/Eu) and $\beta$ (Nd/Eu), are obviously enhanced in the IL system compared to that in the n-dodecane system. The high selectivity of Dy over Nd in the IL system is favorable for the separation and recycling of the metals from a magnetic material containing Dy and Nd.

3.2. Synergistic extraction of rare-earth ions in [C$_8$mim][Tf$_2$N]

The synergistic extraction of the rare-earth ions with a mixture of HO8Q and TOPO, TBP or LIX63 in the [C$_8$mim][Tf$_2$N], was examined. As shown in Figure 4, the extraction performance of HO8Q for the

![Figure 4](image1.png)

Figure 4. Synergistic extraction with HO8Q and co-extractant in [C$_8$mim][Tf$_2$N]. HO8Q: 10 mM and co-extractant: 10 mM. pH$_0$ = 6.5.

![Figure 5](image2.png)

Figure 5. Effect of TOPO concentration on the extraction of metal ions with HO8Q. HO8Q: 10 mM. pH$_0$ = 6.5.
rare-earth ions was notably enhanced in the presence of the co-extractant TOPO. Here, TOPO (10 mM) alone in [C$_8$ mim][Tf$_2$N] did not show any extraction ability for the rare-earth ions from the feed aqueous phases containing 0.1 M nitrate ion, and the enhancement of extraction ability is attributed to a synergistic effect.

The synergistic extraction of the rare-earth ions with a mixture of HO8Q and TOPO, TBP or LIX63 in the [C$_8$mim][Tf$_2$N], was examined. As shown in Figure 4, the extraction performance of HO8Q for the rare-earth ions was notably enhanced in the presence of the co-extractant TOPO. Here, TOPO (10 mM) alone in [C$_8$mim][Tf$_2$N] did not show any extraction ability for the rare-earth ions from the feed aqueous phases containing 0.1M nitrate ion, and the enhancement of extraction ability is attributed to a synergistic effect.

The effect of the concentration of the synergistic ligand TOPO on the distribution ratio of the rare-earth ions is shown in Figure 5. A linear relationship with a slope close to 1 was obtained for each metal ion in the IL and n-dodecane systems. This indicates the extracted complex contains one TOPO molecule.

The other co-extractants TBP and LIX63 showed an insignificant effect on the extraction ability of HO8Q, although they have improved a little the extraction performance for the heavy rare earth, Dy.

4. Conclusion

In this study, it was found that HO8Q can extract rare-earth ions at pH values greater than 5.5. Higher extraction efficiency for a heavy rare earth, Dy, was observed in the IL system compared to that in the n-dodecane system, whereas the extraction ability of the IL system for a light rare earth, Nd, decreased compared to that in the n-dodecane system, thus the IL system gave a better selectivity between Dy and Nd ($\beta$: 108). In the extraction process, a visible change from colorless to light yellow can be observed in the extracting phase. Furthermore, it is worth mentioning that TOPO can effectively improve the extraction ability of rare earth ions as a co-extractant in the IL system. It was confirmed that the extracted complex contains one molecule of the synergistic ligand TOPO.

References