Application of Propylene Carbonate to Liquid-Liquid Extraction of Metal Ion

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Abstract

4-Methyl-1,3-dioxolan-2-one is well known solvent in the name of propylene carbonate (PC) and has good solvent properties, e.g. low toxicity, less flammable, high density and less viscous, nevertheless the application of PC in solvent extraction has only been considered in a few cases. Then, availability of PC to solvent extraction was examined by applying it to the extraction of three different kinds of analyte, hydrophilic neutral species, a chelate and an ion association complex. At first, 6 water miscible solvents, i.e., methanol, isopropanol, tert-butanol, acetone, acetonitrile and tetrahydrofuran were arbitrarily selected as hydrophilic neutral species and the extractability of PC and cyclohexane for these solvents were examined. Dioctyldiglycolamic acid (Abbreviate as DODGAA) complex of lanthanide (Ln³⁺) was chosen as an example of chelate extraction and was extracted with PC and n-hexane, respectively. Ion association extraction was investigated with the extractability of bis(1,10-phenanthroline) iron(II) complex (Fe(phen)3²⁺²X⁻) by using PC, toluene and nitrobenzene. In all cases, PC showed the significant extractability compared to common solvents.

Keywords: propylene carbonate, dioctyldiglycolamic acid, lanthanide, bis(1,10-phenanthroline) iron(II)

1. Introduction

Recently, the recovery of valuable minor elements from urban mining has attract much attention due to exhaustion of natural resources, and the significance of liquid-liquid extraction is increasing in this area. New solvents having useful function with low toxicity, smell and irritation to the eyes or skin is required to further develop this application. PC is a well-known solvent and is comparatively safe with a high flash point, 132°C. PC is also considered to be less toxic and environment-friendly since it has no halogen atoms and aromatic ring in a molecule. Nevertheless, only limited applications of PC to metal extraction had been reported. Murata et al., reported the homogeneous liquid-liquid extraction method for the extraction of Mo(IV)5) and Fe(III) thienoyltrifluoro acetonate5) by utilizing the upper critical solution temperature of PC at 72 °C. Moreover, PC has important character as an extraction solvent as it is polar and heavy having specific gravity 1.207(at 20 °C)3). Stephens et al., utilized PC to extraction photometric determination of ferroin-type Fe(II) complexes instead of nitrobenzene3-6). After these work, PC has seen little use. The potential of PC as an extraction solvent has not been evaluated sufficiently. Then, in order to investigate the ability of PC as an extraction solvent, the present study was carried out with the arbitrarily selected species, e.g., hydrophilic solvents as an example for neutral compound, Fe(phen)3²⁺²X⁻ as that for ion association complex and DODGAA complexes of Ln³⁺ as representative of chelate.

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complex, by comparing it’s extractability with those of usual solvents.

2. Methodology

2.1 Reagents

PC was purchased from Kanto Chemical Co., Inc. and used without further purification. All other reagents were of analytical reagent grade and were used as received.

2.2 Extraction procedure for hydrophilic compounds

Methanol, isopropanol, tert-butanol, acetone, acetonitrile and tetrahydrofuran were dissolved in water at a concentration of 10% for aqueous phase. An equal volume of the aqueous and organic phases were shaken vigorously for 1 h, and phases were separated by centrifuge for 20 min. The amount of the extracted species was determined by using gas chromatograph (Hitachi model G6000) equipped with the column packing Porapak Q and TCD.

2.3 Extraction of Ln³⁺ with DODGAA

DODGAA was mainly used as chelate extractant in this study. The extraction was carried out according to the batch method at 25±1°C in a similar manner to the previous study. Three milliliter of the aqueous phase containing 1.0 mmol/l Ln³⁺ as a chloride was equilibrated with same volume of organic phase containing 10 mmol/l DODGAA by shaking vigorously for 1 h. Incidentally, since n-hexane could not dissolve DODGAA well, 1-octanol was added to n-hexane in the ratio of 5% in order to improve the solubility. After phase separation, 2ml of the organic phase was shaken with 2 ml of 3 mol/l HCl to back-extract Ln³⁺. The concentration of Ln³⁺ was determined by ICP-OES (Varian Vista Pro).

2.4 Extraction of Fe(phen)³⁺ complex ion

Ion association complexes of 1.25 mmol/l bis(1,10-phenanthroline) iron(II) complex cation with 7 kinds of anion such as F⁻, Cl⁻, Br⁻, I⁻, NO₃⁻, SCN⁻ and CH₃COO⁻ (Fe(phen)³⁺2X⁻) were extracted at pH 5.0 by the conventional method.

Toluene, nitrobenzene and PC were used for the organic phase.

2.5 Determination of percent extraction

PC is somewhat water soluble, and then the volume of PC decreased by 10% while that of aqueous phase increased by 10% after equilibration on the average. However, the effect of this volume change on the percent extraction (E(%)) was cancelled by using [Ln³⁺]₀ instead of [Ln³⁺]₀ for the calculation of E(%), where [Ln³⁺]₀ is the concentration of Ln³⁺ in the aqueous phase equilibrated with PC and [Ln³⁺]₀ is that in the prepared solution. Practically, the difference between corrected and uncorrected value of E% with volume change was negligibly small, so that E% was obtained without considering the volume change in this study.

3. Results and Discussion

3.1 Extraction of hydrophilic compounds

In order to evaluate the extractability of PC, 6 solvents were selected as a hydrophilic sample and were extracted with PC as well as cyclohexane which is a representative non-polar solvent. As shown in Fig. 1, PC can extract 5 solvents with better E(%) than cyclohexane except for tetrahydrofuran and clearly shows the significant extractability for the hydrophilic species. The dielectric constant (ε) of methanol, isopropanol, tert-butanol, acetone, acetonitrile and tetrahydrofuran are 33.1, 22.2, 11.4, 20.7, 37.5 and 7.58, respectively. In the cyclohexane extraction, weak positive correlation (r²=0.503) was obtained between ε value and E(%). While, ε of PC is extraordinary high, 69.0, so that PC could equally extract 6 solvents irrespective of their ε values.

3.2 DODGAA Extraction of Ln³⁺

DODGAA is newly developed extractant and is regarded to be effective for the separation of lanthanides and actinides, the effect of PC on the DODGAA extraction of lanthanides was examined. Figures 2-a and -b show that the extraction of Sc(III) was significantly improved by changing the solvent from n-hexane to PC and the separation of Sc(III) from other Ln³⁺ ions is also improved. In order to indicate the separation between Ln³⁺ ions clearly, the pH values at 50% extraction (pH₁/₂) for Ln³⁺ ions were cited in Table 1. Table 1 indicates that the pH₁/₂ value of Sc(III) shifted from 1.61 to 0.62 by changing solvent from n-hexane to PC and those of Y(III), Dy(III), Er(III) and Yb(III) also decreased slightly. When
the separation of Sc(III) and La(III) and that of Sc(III) and Y(III) are evaluated in terms of the difference of pH\textsubscript{1/2} values (Expressed as \(\Delta \text{pH}_{1/2(Sc-La)}\) and \(\Delta \text{pH}_{1/2(Sc-Y)}\)), \(\Delta \text{pH}_{1/2(Sc-La)}\) value obtained with PC and n-hexane are 2.48 and 1.49 and \(\Delta \text{pH}_{1/2(Sc-Y)}\) values are 1.28 and 0.73, respectively. Consequently, the separations in these two pairs were improved remarkably by changing the solvent from n-hexane to PC.

Here, the pH\textsubscript{1/2} values in n-hexane extraction system obtained in this study did not agree with the reported values. The reason for these discrepancies is mainly attributed to the difference in the Ln\textsuperscript{3+} ion concentration. Due to the limitation on the ICP-OES measurement, metal ion concentration could not be decreased enough and the concentration ratio of [DODGAA]/[Ln\textsuperscript{3+}] became very small in this study with increased error. The same applies to all the slopes of the extraction curves for the other ions. However it is reported that lanthanides were extracted in the form of Ln(DODGAA)\textsubscript{3} in the DODGAA extraction system\textsuperscript{9), it is expected that the pH\textsubscript{1/2} values in n-hexane extraction system and the slopes of extraction curves would agree with those cited in Ref. 9 by using a large enough concentration ratio of [DODGAA]/[Ln\textsuperscript{3+}].

### 3.3 Effect of solvent on the extraction of Fe(phen)\textsubscript{3}\textsuperscript{2+2X-}

Fe(phen)\textsubscript{3}\textsuperscript{2+2X-} was selected as an example of ion association complex and was extracted with nitrobenzene, toluene and PC. The A value is a factor of the extractability for anion which was proposed by Motomizu\textsuperscript{10) and correlates to the ionic radius of corresponding anion (Table 2). Figure 3 shows the correlation between A value and percent extraction of Fe(phen)\textsubscript{3}\textsuperscript{2+2X-}. In the ion

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**Table 1 pH\textsubscript{1/2} value of Ln\textsuperscript{3+}.**

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>PC\textsuperscript{a)</th>
<th>Hexane\textsuperscript{b)</th>
<th>Hexane\textsuperscript{c}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc\textsuperscript{3+}</td>
<td>0.62</td>
<td>1.61</td>
<td>-</td>
</tr>
<tr>
<td>Y\textsuperscript{3+}</td>
<td>1.90</td>
<td>2.34</td>
<td>-</td>
</tr>
<tr>
<td>La\textsuperscript{3+}</td>
<td>3.10</td>
<td>3.10</td>
<td>2.46</td>
</tr>
<tr>
<td>Dy\textsuperscript{3+}</td>
<td>1.63</td>
<td>2.10</td>
<td>1.44</td>
</tr>
<tr>
<td>Er\textsuperscript{3+}</td>
<td>1.59</td>
<td>2.06</td>
<td>1.44</td>
</tr>
<tr>
<td>Yb\textsuperscript{3+}</td>
<td>1.61</td>
<td>1.93</td>
<td>1.37</td>
</tr>
</tbody>
</table>

a) and b): Present study. [Ln\textsuperscript{3+}]\textsubscript{i0}=1.0 mmol/l, [DODGAA]\textsubscript{i0}=10 mmol/l.

c) Read data from the figure cited in the Ref. 9.

\([M^{3+}] = 0.01 \text{ mmol/l}, [DODGAA] = 10 \text{ mmol/l}.\)

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**Table 2 The A value of anion.**

<table>
<thead>
<tr>
<th>Anion</th>
<th>A value</th>
</tr>
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<tbody>
<tr>
<td>F\textsuperscript{-}</td>
<td>-11.06</td>
</tr>
<tr>
<td>Cl\textsuperscript{-}</td>
<td>-8.08</td>
</tr>
<tr>
<td>Br\textsuperscript{-}</td>
<td>-6.89</td>
</tr>
<tr>
<td>I\textsuperscript{-}</td>
<td>-5.32</td>
</tr>
<tr>
<td>SCN\textsuperscript{-}</td>
<td>-5.17</td>
</tr>
<tr>
<td>NO\textsubscript{3}\textsuperscript{-}</td>
<td>-7.05</td>
</tr>
<tr>
<td>CH\textsubscript{3}COO\textsuperscript{-}</td>
<td>-9.79</td>
</tr>
</tbody>
</table>
association extraction system, the polarity of solvent affects greatly to the extractability of analyte, and therefore, nitrobenzene of which dielectric constant is 34.83 is mainly used for the extraction of Fe(phen)$_3$$^{2+}$X$^-$. Although both PC and nitrobenzene gave the same good log D value for the extractable anions, SCN$^-$ and I$^-$, PC showed the better extractability compared with nitrobenzene for the less extractable and hydrophilic anions. It can be considered that higher dielectric constant of PC, 65.1$^3$, than that of nitrobenzene brought about the better results.

4. Conclusion

The present study has revealed that PC has a unique function to extract hydrophilic neutral species of which cyclohexane cannot extract. PC showed the better extractability for Fe(phen)$_3$$^{2+}$X$^-$ containing hydrophilic anion compared with nitrobenzene and the excellent separability for Sc(III) and La(III), and Sc(III) and Y(III) in DODGAA extraction system. Thus, it can be concluded that PC is not only non-toxic, environment-friendly, dense, no unpleasant smell but also has function and good utility in both chelate and ion association extraction system.

References

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