Highly Effective Extraction of Ruthenium from Hydrochloric Acid Solutions with a Protic Ionic Liquid Trioclylammonium Chloride

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Extraction of ruthenium(III) from hydrochloric acid solutions was investigated at 25°C by using a protic ionic liquid, trioclylammonium chloride ([HTOA]Cl), as an extraction solvent. Extraction percentages of more than 99% were obtained under the following conditions: volume ratio of aqueous to ionic liquid phase = 1; shaking time ≥ 12 h; aqueous HCl concentration (C_{HCl}) = 4.0 mol/L. The D vs. C_{HCl} plot shows a bell-shaped curve with the maximum D = 106 at C_{HCl} = 4.0 mol/L. Several other ionic liquids were also examined as extraction solvents, and trihexyltetradecylphosphonium chloride ([THTDP]Cl) was found to have a higher extraction efficiency (D = 8 × 10^2 at C_{HCl} = 4.0 mol/L) than [HTOA]Cl. By using 1.0 mol/L aqueous thiourea as a stripping solution, 100% of the metal was back-extracted from [HTOA]Cl, whereas only 21.4% was back extracted from [THTDP]Cl. The possibility of extraction separation of ruthenium(III) from other metals was also investigated.

1. Introduction

Ruthenium is an important platinum group element which has a wide variety of application in diverse fields such as electronics, medicine, catalysis, biology, nanoscience, redox, and photoactive materials [1]. In the refining and recovering processes of Ru, the metal is generally oxidized to volatile Ru^{VIII}O_4 and separated by distillation. The oxidation and distillation method, however, has problems such as that the generated RuO_4 is unstable and highly corrosive because the stable oxidation state of Ru is generally +3. Solvent extraction, which is an effective separation method for other platinum group elements such as Pd and Pt, is generally ineffective for Ru. For the extraction of Ru^{III} from chloride media, various extraction systems have been investigated using methyltrioclylammonium chloride [2], industrial extractants (e.g., Alamine 336, Aliquat 336, and LIX54) [3,4], dihexyl sulfoxide [5], N,N'-dimethyl-N,N'-dicyclohexylmalonamide [6], N-2-ethylhexyl-bis(N-di-2-ethylhexyl-ethylamidine)amine [7], and tetraalkylphosphonium-based ionic liquids [8,9]. However, the distribution ratio reported for Ru^{III} is 10 to 30 at most, indicating that quantitative extraction is difficult. In addition, all the extractants have been used as mixtures with organic molecular solvents, which leads to health, safety, and environmental problems. We previously reported that the use of protic ammonium-based ionic liquids without dilution is effective for the extraction of anionic chloro complexes of metal ions [10-12]. Ionic liquids (ILs) are hardly volatile and recognized as green solvents. Thus, in this study, we examined the extraction behavior of Ru^{III}
from hydrochloric acid solutions with trioctylammonium chloride ([HTOA]Cl). Several other ILs, trihexyltetradecylphosphonium chloride ([THTDP]Cl), methyltrioctylammonium chloride ([MTOA]Cl), tris(2-ethylhexyl)ammonium chloride ([HTEHA]Cl), and trioctylammonium bis(trifluoromethanesulfonyl)-imide ([HTOA][NTE]) were also examined for comparison. Moreover, the possibilities of back-extraction of RuIII from the IL phase and separation of RuIII from other metals were investigated.

2. Experimental

2.1 Reagents and instruments

Water was deionized and further purified through a Simplicity UV system (Millipore). [HTOA]Cl was prepared by vigorously mixing 3 mol/L hydrochloric acid (Kanto Chemicals, UGR) and trioctylamine (Sigma-Aldrich, >98%) purified by vacuum distillation in a volume ratio of 1:1. The product was washed with water, dried under vacuum on P2O5 for more than 24 h, recrystallized from distilled hexane, and dried again under vacuum for more than 8 h. [HTOA][NO3] was prepared in a similar manner from 3 mol/L nitric acid (Kanto Chemicals, UGR) and trioctylamine, and purified by recrystallization from distilled cyclohexane. The purified [HTOA]Cl and [HTOA][NO3] were white crystals which became liquids after saturation with water. [HTEHA]Cl was prepared in a similar manner from 3 mol/L hydrochloric acid and vacuum-distilled tris(2-ethylhexyl)amine (Sigma-Aldrich, >97%), but recrystallization could not be performed. [HTOA][NTE] was prepared according to a previous study [10]. [MTOA]Cl (Sigma-Aldrich, >97.0%) and [THTDP]Cl (Kanto Chemicals, >95%) were purchased and used after washing with water for several times. An aqueous solution of RuIII was purchased as a 1000 ppm atomic absorption standard solution (5% HCl) from Sigma-Aldrich. Aqueous solutions of AlIII, TiIV, V (probably, a mixture of VV and VIV), FeIII, CoII, NiII, CuII, ZnII, MoVI, WVI, and PtIV were also commercial atomic absorption standards from Wako Pure Chemical (Al, Co, Cu, and Pt) and Kanto Chemicals (the other metals). Aqueous solutions of CrIII and NdIII were prepared by dissolving CrCl3•6H2O (Wako Pure Chemical, 99.5%) and Nd2O3 (Kanto Chemicals, 99.95%) in 1 mol/L hydrochloric acid. All other reagents were obtained from commercial sources as guaranteed or extra-pure grade and used without further purification.

The measurements of density, viscosity, and water content of water-saturated ILs were performed with an Anton Paar DMA35n oscillating U-tube density meter, a Kusano No.2B Ubbelohde-type glass viscometer (viscometer constant: 2.919 nm2·s−2), and a Hiranuma AQ-7 Karl Fischer titrator, respectively. The shaking and centrifugation of a centrifuge tube were carried out using a Taitec SR-1N reciprocal shaker (200 strokes/min) and a Kubota 2010 tabletop centrifuge (3000 rpm) with an RS-240 swing rotor, respectively. The accuracy of the temperature was ± 0.05°C for the viscosity measurements and ± 0.2°C for the density and water content measurements and the extraction experiments. The Ru concentrations in aqueous samples were generally determined with a Hitachi Z-5700 polarized Zeeman atomic absorption spectrophotometer in the graphite furnace mode. An PerkinElmer Avio500 ICP optical emission spectrometer and a Shimadzu DSC-60 Plus differential scanning calorimeter were used for the determination of multiple metals and for the measurement of thermochemical properties of ILs, respectively.

2.2 Extraction of Ru

Aqueous solutions containing 1.0 mol/L to 8.0 mol/L HCl and 4.0 × 10−5 mol/L to 4.9 × 10−3 mol/L RuIII were prepared and stored for 72 h or more at room temperature to obtain reproducible results. Equal
volumes of the aqueous solution and a water-saturated IL were placed in a PP centrifuge tube. The two-phase mixture was mechanically shaken for 1 h to 24 h in a thermostatic chamber at 25°C. After phase separation by centrifugation, the concentration of Ru(III) in the aqueous phase was determined by atomic absorption spectrophotometry. The concentration of Ru(III) in the IL phase was calculated based on the mass balance. The distribution ratio \( D \) defined as the ratio of molar concentration in the IL phase to that in the aqueous phase and the forward-extraction percentage \( \% E \) were calculated.

Back-extraction of Ru(III) was also conducted as follows. An aliquot of the IL phase after the forward extraction was transferred to another centrifuge tube, to which an equal volume of stripping solution (water, 1.0 mol/L aqueous thiourea, 1.0 mol/L aqueous nitric acid, or concentrated hydrochloric acid) was added. The mixture was mechanically shaken for 15 min to 24 h at 25°C and centrifuged. The concentration of Ru(III) in the stripping phase was determined and the back-extraction percentage \( \% E_{\text{back}} \) was calculated.

2.3 Extraction of multiple metals

An aqueous solution containing 4.0 mol/L HCl and \( 5.0 \times 10^{-4} \) mol/L Al(III), Ti(IV), V, Cr(III), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Mo(VI), Ru(III), Nd(III), W(VI), and Pt(IV) was prepared and stored for 72 h at room temperature. Equal volumes of the aqueous solution and a water-saturated IL were placed in a centrifuge tube, and the mixture was mechanically shaken for 18 h at 25 ± 0.2°C. After centrifugation, an aliquot of the IL phase was transferred into another centrifuge tube together with an equal volume of water. The mixture was shaken for 1 h at 25°C and centrifuged. An aliquot of the IL phase was transferred again into another centrifuge tube in which an equal volume of a 1.0 mol/L aqueous thiourea solution was placed. The mixture was shaken for 21 h at 25°C and centrifuged. The concentration of each metal in each aqueous phase was determined by ICP optical emission spectroscopy, and the extraction percentages in the forward- \( \% E \) and back-extractions \( \% E_{\text{back}} \) were calculated for each metal.

3. Results and Discussion

3.1 Fundamental properties of ILs

The melting points (mp) of dry and water-saturated [HTOA]Cl, as determined by visual observation, were 72°C and 22°C, respectively. To obtain more detailed thermal properties, differential scanning calorimetry (DSC) was performed for [HTOA]Cl (7 mg) sealed in an Al pan under flowing nitrogen with a heating/cooling rate of 5 °C min⁻¹ in the temperature range –10°C to 90°C. To eliminate the thermal history, two heating and cooling cycles of scans were done and the data in the second cycle was analyzed. The mp and freezing point (fp) determined were as follows: mp = 72.0°C to 74.1°C and fp = 62.6°C to 64.4°C for dry [HTOA]Cl; mp = 21.1°C to 23.2°C and fp = 6.2°C to 6.8°C for water-saturated [HTOA]Cl. Both the mp and fp values of the IL are lowered remarkably by dissolution of water. The water content in water-saturated [HTOA]Cl at 25°C, as determined by Karl Fischer titrations, was 7.6 mass%.

The DSC measurements under similar conditions, but in the temperature range –130°C to 50°C, were also conducted for [HTEHA]Cl. The values mp = –16.2°C to –14.2°C and fp = –24.0°C to –23.3°C were obtained for dry [HTEHA]Cl, whereas water-saturated [HTEHA]Cl was liquid or glass in the above temperature range; the glass-transition point was evaluated to be –86.2°C. Although [HTOA]Cl and [HTEHA]Cl are constitutional isomers of each other, the latter bearing branched alkyl groups in the cation are difficult to crystallize compared to the former with linear ones.
The density and viscosity values at 25°C of all six water-saturated ILs are summarized in Table 1. Some of the data were determined in this study, and the others are cited from the literature [10,12,13]. The viscosity of [HTOA]Cl is higher than those of [MTOA]Cl and [THTDP]Cl, comparable to that of [HTOA][NTf2], and lower than those of [HTOA][NO3] and [HTEHA]Cl. As seen from the comparison of the isomers, [HTEHA]Cl and [HTOA]Cl, the branched alkyl groups of [HTEHA] + are responsible for the high viscosity of [HTEHA]Cl. The densities at 25°C of [HTOA]Cl, [HTETA]Cl, and [THTDP]Cl were also determined after the ILs were equilibrated with 4.0 mol/L hydrochloric acid; the values are 0.8986 ± 0.0001 g/cm3 for [HTOA]Cl, 0.9158 ± 0.0001 cm3/L for [HTETA]Cl, and 0.9181 ± 0.0000 g/cm3 for [THTDP]Cl. The density change from the IL saturated with water to that equilibrated with a 4.0 mol/L hydrochloric acid is negligibly small (only 4% or less). Therefore, the volume of the IL phase in each extraction experiment was calculated from the mass using the density of the water-saturated IL shown in Table 1. In addition, the volume change of the IL phase due to dissolution of IL to the aqueous phase was neglected because of the very low solubility in water; the aqueous solubilities at 25°C are 3.94 × 10 −4 mol/L for [HTOA]Cl [12], 2.821 × 10 −4 mol/L for [HTOA][NO3] [12], 6.3 × 10 −6 mol/L for [HTOA][NTf2] [10], 5.57 × 10 −3 mol/L for [MTOA]Cl [12], and (0.2 - 1.5) × 10 −4 mol/L for [THTDP]Cl [14]; the solubility of [HTEHA]Cl is unknown but probably comparable to that of the isomer, [HTOA]Cl.

### 3.2 Extraction behavior of Ru from hydrochloric acid to ILs

First, the effect of the shaking time for the extraction on the extractability of RuIII was investigated. The initial concentrations of HCl and RuIII in the aqueous phase were fixed to 4.0 mol/L and 1.0 × 10 −4 mol/L, respectively. In Figure 1, the log D value is plotted against the shaking time. Owing to the slow ligand-exchange properties of RuIII, the D value increases slowly with an increase of shaking time; it reaches 100 with a shaking time of 12 h and becomes nearly constant when the shaking time is 18 h or longer. Therefore, the shaking time was fixed to 18 h in the following extraction experiments.

The effect of initial aqueous HCl concentration (C_{HCl}) on the extractability of RuIII was investigated.

| IL        | ρ (g/cm3)  | η (mPa·s) |
|-----------|------------|-----------|
| [HTOA]Cl  | 0.8905 ± 0.0001 | 183.0 c   |
|           | 0.8903 c   |           |
| [HTOA][NO3] | 0.9186 c  | 267.1 c   |
| [HTOA][NTf2] | 1.1018 d  | 179.4 d   |
| [MTOA]Cl  | 0.9206 c   | 85.4 c    |
| [HTEHA]Cl | 0.8792 ± 0.0000 | 775.0 ± 1.2 |
| [THTDP]Cl | 0.9037 ± 0.0000 | 134.72 e  |

|              |              |            |
| [HTOA]+ = trioctylammonium, [MTOA]+ = methyltrioctylammonium, [HTEHA]+ = tris(2-ethylhexyl)ammonium, [THTDP]+ = trihexyltetradecylphosphonium. |
| Each uncertainty represents the standard error of the mean from 3 to 5 independent experiments. |
| c Ref. 12. |
| d Ref. 10. |
| e Ref. 13. |

The density and viscosity values at 25°C of all six water-saturated ILs are summarized in Table 1. Some of the data were determined in this study, and the others are cited from the literature [10,12,13]. The viscosity of [HTOA]Cl is higher than those of [MTOA]Cl and [THTDP]Cl, comparable to that of [HTOA][NO3], and lower than those of [HTOA][NO3] and [HTEHA]Cl. As seen from the comparison of the isomers, [HTEHA]Cl and [HTOA]Cl, the branched alkyl groups of [HTEHA] + are responsible for the high viscosity of [HTEHA]Cl. The densities at 25°C of [HTOA]Cl, [HTETA]Cl, and [THTDP]Cl were also determined after the ILs were equilibrated with 4.0 mol/L hydrochloric acid; the values are 0.8986 ± 0.0001 g/cm3 for [HTOA]Cl, 0.9158 ± 0.0001 cm3/L for [HTETA]Cl, and 0.9181 ± 0.0000 g/cm3 for [THTDP]Cl. The density change from the IL saturated with water to that equilibrated with a 4.0 mol/L hydrochloric acid is negligibly small (only 4% or less). Therefore, the volume of the IL phase in each extraction experiment was calculated from the mass using the density of the water-saturated IL shown in Table 1. In addition, the volume change of the IL phase due to dissolution of IL to the aqueous phase was neglected because of the very low solubility in water; the aqueous solubilities at 25°C are 3.94 × 10 −4 mol/L for [HTOA]Cl [12], 2.821 × 10 −4 mol/L for [HTOA][NO3] [12], 6.3 × 10 −6 mol/L for [HTOA][NTf2] [10], 5.57 × 10 −3 mol/L for [MTOA]Cl [12], and (0.2 - 1.5) × 10 −4 mol/L for [THTDP]Cl [14]; the solubility of [HTEHA]Cl is unknown but probably comparable to that of the isomer, [HTOA]Cl.

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The effect of initial aqueous HCl concentration (C_{HCl}) on the extractability of RuIII was investigated.
The log $D$ vs. $C_{\text{HCl}}$ plot is shown in Figure 2. The plot is a bell-shaped curve; the maximum value of $D$ is 106 ($%E = 99.1$) when $C_{\text{HCl}} = 4.0$ mol/L. The $D$ value is the highest reported so far for Ru$^{III}$.

Suzuki et al. [7] investigated the species distribution of Ru$^{III}$-chloro complexes, $[\text{RuCl}_n(\text{H}_2\text{O})_{6-n}]^{3-n}_n$ ($n = 3 - 6$), in hydrochloric acid solutions. According to that, anionic $[\text{RuCl}_4(\text{H}_2\text{O})_2]^-$, $[\text{RuCl}_5(\text{H}_2\text{O})]^2-$, and $[\text{RuCl}_6]^3-$ are dominant in the $C_{\text{HCl}}$ range 0.5 - 2 mol/L, 3 - 7 mol/L, and 8 - 10 mol/L, respectively. Since ILs have a feature that they extract ionic species by ion-pair transfer and ion exchange mechanisms [15-17], the following two extraction reactions can be proposed for the extraction of Ru$^{III}$ with $[\text{HTOA}]\text{Cl}$:

$$[\text{RuCl}_n(\text{H}_2\text{O})_{6-n}]^{3-n}_n + (n - 3) [\text{HTOA}]^+_w \rightleftharpoons [\text{RuCl}_n(\text{H}_2\text{O})_{6-n}]^{3-n}_n + (n - 3) [\text{HTOA}]^+_\text{IL} \quad (1)$$

$$[\text{RuCl}_n(\text{H}_2\text{O})_{6-n}]^{3-n}_n + (n - 3) \text{Cl}^-_w \rightleftharpoons [\text{RuCl}_n(\text{H}_2\text{O})_{6-n}]^{3-n}_n + (n - 3) \text{Cl}^-_\text{IL} \quad (2)$$

where the subscripts ‘IL’ and ‘w’ refer to the IL and aqueous phases, respectively. These reactions are not independent but mutually related through the solubility product of the reaction, $[\text{HTOA}]\text{Cl}_{\text{IL}} \rightleftharpoons [\text{HTOA}]^+_w + \text{Cl}^-_w$. According to Eq. (2), an increase of aqueous Cl$^-$ concentration has a negative effect on the extraction of each anionic complex. From the above, the $C_{\text{HCl}}$ dependence of $D$ (Figure 2) suggests that the most probable extracted species is $[\text{RuCl}_5(\text{H}_2\text{O})]^2-$.

The dependence of log $D$ on the initial aqueous concentration of Ru$^{III}$ was also investigated at $C_{\text{HCl}} = 4.0$ mol/L. In the Ru$^{III}$ concentration range between $4.0 \times 10^{-5}$ mol/L and $4.9 \times 10^{-3}$ mol/L, the $D$ value was nearly constant, supporting that the metal is extracted as a mononuclear complex.

Extraction abilities of the six water-saturated ILs for Ru$^{III}$ were investigated and compared. The initial aqueous concentrations of HCl and Ru$^{III}$ were 4.0 mol/L and $1.0 \times 10^{-4}$ mol/L, respectively. The log $D$ and %$E$ values are summarized in Table 2. The extraction efficiency varies in the following sequences: for the Cl$^-$-based ILs, $[\text{THTDP}]\text{Cl} > [\text{HTOA}]\text{Cl} \approx [\text{HTEHA}]\text{Cl} \gg [\text{MTOA}]\text{Cl}$; for the $[\text{HTOA}]^+$-based ILs, $[\text{HTOA}]\text{Cl} > [\text{HTOA}]\text{[NO}_3^-] \gg [\text{HTOA}]\text{[NTf}_2^-]$. Only $[\text{THTDP}]\text{Cl}$ shows a higher extraction efficiency than $[\text{HTOA}]\text{Cl}$. In general, the extractability of an anion increases with an increase of hydrophobicity of
the IL cation and of hydrophilicity of the IL anion [16,17]. The IL sequences of the extraction efficiency are reasonably consistent with those expected from the aqueous solubilities of the ILs described above. The much higher extractability of [HTOA]Cl compared to [MTOA]Cl may suggest a specific interaction such as hydrogen bonding between the protic cation ([HTOA]+) and the anionic RuIII-chloro complex.

3.3 Back-extraction of Ru from ILs

Back-extraction of RuIII from the [HTOA]Cl phase was examined by using several aqueous stripping solutions. The IL/aqueous volume ratio and the shaking time for the back-extraction were kept constant at 1 and 2 h, respectively. The %E values determined for water, 1.0 mol/L aqueous thiourea, 1.0 mol/L aqueous HNO3, and concentrated hydrochloric acid (12 mol/L HCl) as stripping solutions were 1.5, 56, 0.56, and 74.3, respectively. Ru was hardly back-extracted with water and 1.0 mol/L HNO3.

The effect of the shaking time for the back-extraction with 1.0 mol/L thiourea or 12 mol/L HCl was evaluated. The %E value with 12 mol/L HCl became a constant value of 74 when the shaking time is 1 h or longer; therefore, quantitative back-extraction was impossible with 12 mol/L HCl. On the other hand, the %E value with 1.0 mol/L thiourea increased gradually with an increase of shaking time; quantitative back-extraction (%E = 100) was achieved with a shaking time of 21 h or longer.

Back-extraction experiments from [HTEHA]Cl and [THTDP]Cl were also conducted by using 1.0 mol/L thiourea with the shaking time of 21 h. The %E values obtained were 95 and 21.4 for [HTEHA]Cl and [THTDP]Cl, respectively. Back-extraction of Ru is possible from [HTEHA]Cl but difficult from [THTDP]Cl.

3.4 Application to a hydrochloric acid solution containing multi metals

The conditions optimized for the forward- and back-extraction of RuIII were applied to the 4.0 mol/L hydrochloric acid solution containing AlIII, TiIV, V, CrIII, FeIII, CoII, NiII, CuII, ZnII, MoVI, RuIII, NdIII, WVI, and PtIV (5 × 10⁻⁴ mol/L for each) which are often included in electronic components. Here, a back-extraction process with water (shaking time = 1 h) was interposed between the forward-extraction with [HTOA]Cl and the back-extraction with 1.0 mol/L aqueous thiourea in order to remove some metals and HCl in the IL phase. The volume ratio of the IL phase to the aqueous phase was fixed to 1 in all the extraction processes. For each metal, the % value in the forward-extraction process and the %E values

| IL         | D      | %E    |
|------------|--------|-------|
| [HTOA]Cl   | 106 ± 3 b | 99.1  |
| [HTOA][NO₃] | 51    | 98.1  |
| [HTOA][NTf₂] | 0.162 | 13.9  |
| [MTOA]Cl   | 2.97   | 74.8  |
| [HTEHA]Cl  | 90.2   | 98.9  |
| [THTDP]Cl  | 8 × 10² | 99.9  |

a Volume ratio of aqueous to IL phase = 1.
b Mean and standard error values from 7 independent measurements.
Table 3. Forward-extraction percentages (%$E$) of metal ions with [HTOA]Cl from 4.0 mol/L hydrochloric acid and back-extraction percentages (%$E_{\text{back}}$) in the subsequent back-extraction processes with water and 1.0 mol/L aqueous thiourea.

| Metal | %$E$ | %$E_{\text{back}}$<sup>b</sup> Water | %$E_{\text{back}}$ 1.0 mol/L thiourea |
|-------|------|-------------------------------------|-------------------------------------|
| Al<sup>III</sup> | 0 | --- | --- |
| Ti<sup>IV</sup> | 0 | --- | --- |
| V | 51.8 | 29 | 62 |
| Cr<sup>III</sup> | 0 | --- | --- |
| Fe<sup>III</sup> | 100 | 0 | 100 |
| Co<sup>II</sup> | 95.4 | 99 | --- |
| Ni<sup>II</sup> | 0 | --- | --- |
| Cu<sup>II</sup> | 99.7 | 38.5 | 47 |
| Zn<sup>II</sup> | 99.8 | 0.5 | 3.4 |
| Mo<sup>VI</sup> | 99.8 | 19 | 0 |
| Ru<sup>III</sup> | 99.5 | 0.2 | 99.9 |
| Nd<sup>III</sup> | 0 | --- | --- |
| W<sup>VI</sup> | 80.2 | 5.8 | 2 |
| Pt<sup>IV</sup> | 99.8 | 0.1 | 99.9 |

<sup>a</sup> Volume ratio of aqueous to IL phase = 1 for all the extraction processes.

<sup>b</sup> Calculated as the ratio of the metal amount in the aqueous phase after the back extraction to that in the IL phase after the forward-extraction.

in the back-extraction processes were determined and are summarized in Table 3. Ru<sup>III</sup> is quantitatively extracted from 4.0 mol/L hydrochloric acid with [HTOA]Cl, hardly back-extracted with water, and quantitatively back-extracted with 1.0 mol/L aqueous thiourea, as in the case of the single metal system. Al<sup>III</sup>, Ti<sup>IV</sup>, Cr<sup>III</sup>, Ni<sup>II</sup>, and Nd<sup>III</sup> are not extracted at all with [HTOA]Cl. Other metals are extracted partially or completely with [HTOA]Cl; Co<sup>II</sup> in the IL phase is quantitatively removed with water; Zn<sup>II</sup>, Mo<sup>VI</sup>, and W<sup>VI</sup> are hardly back-extracted with the aqueous thiourea solution. Therefore, Ru<sup>III</sup> can be effectively separated from Al<sup>III</sup>, Ti<sup>IV</sup>, Cr<sup>III</sup>, Co<sup>II</sup>, Ni<sup>II</sup>, Zn<sup>II</sup>, Mo<sup>VI</sup>, Nd<sup>III</sup>, and W<sup>VI</sup> through the three extraction processes. On the other hand, a part of V and Cu<sup>II</sup> and all of Fe<sup>III</sup> and Pt<sup>IV</sup> are recovered in the thiourea solution together with Ru<sup>III</sup>, indicating that the separation of Ru<sup>III</sup> from these metals is difficult.

4. Conclusion

Ru<sup>III</sup> in hydrochloric acid can be effectively extracted with a protic IL, [HTOA]Cl. The distribution ratio exceeds 100 although a long shaking time is necessary. No other extraction system with such a high distribution ratio for Ru<sup>III</sup> has been reported. Back-extraction of Ru from the IL phase is also possible with aqueous thiourea solution. Ru<sup>III</sup> can be quantitatively recovered and effectively separated from Al<sup>III</sup>, Ti<sup>IV</sup>, Cr<sup>III</sup>, Co<sup>II</sup>, Ni<sup>II</sup>, Zn<sup>II</sup>, Mo<sup>VI</sup>, Nd<sup>III</sup>, and W<sup>VI</sup> through forward-extraction with [HTOA]Cl from 4.0 mol/L.
hydrochloric acid, back-extraction with water, and back-extraction with 1.0 mol/L thiourea.

[HTEHA]Cl, which is a structural isomer of [HTOA]Cl, is comparable to [HTOA]Cl in the forward- and back-extraction behavior, but the viscosity in the water-saturated state is much higher for [HTEHA]Cl with branched alkyl groups than for [HTOA]Cl with linear ones. A phosphonium-based IL, [THTDP]Cl, has a higher extraction efficiency for Ru$^{III}$ than [HTOA]Cl does, but the back-extraction of Ru$^{III}$ with aqueous thiourea is difficult. [HTOA]Cl also has the following merits: it can be easily prepared by simple acid-base reactions of trioctylamine with HCl and easily purified by recrystallization; the viscosity in the water-saturated state is not so high and the aqueous solubility is sufficiently low. It is expected that [HTOA]Cl will be used as an excellent extraction solvent for Ru$^{III}$.

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