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Use of 1-alkyl-3-methylimidazolium hexafluorophosphate room temperature ionic liquids as chelate extraction solvent with 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione

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Abstract

Possible use of room temperature ionic liquids (RTILs) as chelate extraction solvent was evaluated by using 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]), 1-hexyl-3-methylimidazolium hexafluorophosphate ([hmim][PF_6]) and 1-octyl-3-methylimidazolium hexafluorophosphate ([omim][PF_6]). These RTILs showed high extraction performance for divalent metal cations with 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione (Htta). The extracted metals were back-extracted into 1 mol dm^{-3} nitric acid quantitatively. Furthermore, the extracted species were estimated as neutral hydrated complexes $M(tta)_2(H_2O)_n$ (n= 1 or 2) for M = Ni, Cu and Pb and anionic complexes $M(tta)_3{}^-$ for M = Mn, Co, Zn and Cd.

Keywords: Room temperature ionic liquids (RTILs); Chelate extraction; Divalent metal cations; 4,4,4-Trifluoro-1-(2-thienyl)-1,3-butanedione (Htta)

1. Introduction

Liquid–liquid extraction [1–7] is a very effective analytical separation method for the metal species in solution. However, several popular extraction solvents (organic solvents) such as benzene, toluene, chloroform and nitrobenzene are toxic, flammable and volatile, and it has been recommended that their use as solvent should be avoided.

Recently, room temperature ionic liquids (RTILs) have been noted as ‘green’ solvents (at the viewpoint of their non-volatile nature, at least) mainly in organic chemistry and catalytic chemistry [8–13]. Especially, a series of RTILs made from 1-alkyl-3-methylimidazolium cations ($Rmim^+$) and bulky anions such as hexafluorophosphate ($PF_6{}^-$), tetrafluoroborate and bis(trifluoromethylsulfonyl)amide have been assessed as valuable solvents because they have relative air and water stability and favorable viscosity and density as solvents. Furthermore, some of them such as 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) are immiscible with water and, therefore, have possibility to be used as solvents for liquid–liquid extraction, provided that it has been reported that [bmim][PF_6] shows hydrolysis nature slightly [14]. In addition, many RTILs have unique physical and chemical properties as solvents, such as high polarity [15–20] and are expected not only as ‘alternative’ solvents but also as ‘novel’ ones.

Since 1999, several researchers have reported concerning performance of the imidazolium-type RTILs on liquid–liquid extraction of metal cations [21–32]. These reports can be categorized into the following three groups: (a) extraction systems using neutral ligands [21–27], (b) those using neutral ligand modified RTILs [28–30], and (c) those using anionic ligands [31,32]. Groups (a) and (b) seem to be based on commonplace idea that RTILs have much amount of hydropho-

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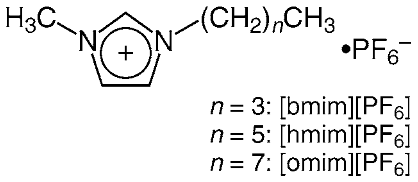

Fig. 1. Chemical structure of [bmim][PF_6], [hmim][PF_6] and [omim][PF_6].

bic anions enough to be used as counterions for ion-pair extraction of cationic metal complexes. However, the idea may be inconsistent with the fact distribution of neutral aromatic carboxylic acids and aniline into RTIL phase is superior to that of respective charged species [33] and that there are hydrogen bonds between the imidazolium cations and the hydrophobic anions in imidazolium-type RTILs [34,35]. In addition, these systems have essential difficulties of back-extraction (stripping) of the extracted metals, which was succeeded only in the limited systems [26,27]. From these facts, use of anionic ligands (group (c)) to form neutral or low-charged metal complexes seems to be preferred in the extraction using RTILs, although the previous studies [34,35] are insufficient at the viewpoint of extraction mechanism research.

In this fundamental study, we researched chelate extraction behavior of divalent transition metal cations using several water-immiscible imidazolium-type RTILs, such as [bmim][PF_6], 1-hexyl-3-methylimidazolium hexafluorophosphate ([hmim][PF_6]) and 1-octyl-3-methylimidazolium hexafluorophosphate ([omim][PF_6]) (Fig. 1), as extraction solvent and 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione (thenoyltrifluoroacetone, Htta), a popular β-diketone-type anionic ligand, as extractant. All of the [Rmim][PF_6] systems showed higher extractability than conventional nitrobenzene, chloroform and toluene systems and these RTILs were able to used as chelate extraction solvent. The metals extracted in [Rmim][PF_6] phase were able to be back-extracted into $1\,\mathrm{mol\,dm^{-3}}$ nitric acid quantitatively. Furthermore, the extracted species were estimated as neutral hydrated complexes $M(tta)_2(H_2O)_n$ ($n = 1$ or 2) for M = Ni, Cu and Pb and anionic complexes $M(tta)_3^-$ for M = Mn, Co, Zn and Cd.

2. Experimental

2.1. Reagents and apparatus

The RTILs [bmim][PF_6], [hmim][PF_6] and [omim][PF_6] were synthesized from respective 1-haloalkane, 1-methylimidazole and hexafluorophosphoric acid according to the method of Huddleston et al. [33] Other chemicals and all solvents were reagent-grade materials and were used without further purification. Distilled deionized water was used throughout.

A Hitachi model Z-6100 polarized Zeeman atomic absorption spectrophotometer was used for the determination of the concentration of a metal in aqueous solution. A Horiba model F-12 pH meter equipped with a Horiba 9510-10D combined glass electrode was used to determine the pH values.

2.2. Distribution of the metals

In a centrifuge tube, an aliquot of an RTIL, nitrobenzene, chloroform or toluene ($1\,\mathrm{cm^3}$) containing $1 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$ of Htta and $5\,\mathrm{cm^3}$ of an aqueous phase containing 1×10^{-5}–$1 \times 10^{-4}\,\mathrm{mol\,dm^{-3}}$ of M^{2+} (M = Mn, Co, Ni, Cu, Zn, Cd or Pb), $1 \times 10^{-1}\,\mathrm{mol\,dm^{-3}}$ of potassium nitrate and $1 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$ of buffer [chloroacetic acid, acetic acid or 2-(N-morpholino)ethanesulfonic acid] were shaken at 25 ± 1 °C for 30 min. After the two phases were separated by centrifugation, the pH and the metal concentration in the aqueous phase were determined and the measured pH was used as equilibrated pH. The metal concentration in the extract phase was determined after back-extraction into 10-fold volume of $1\,\mathrm{mol\,dm^{-3}}$ nitric acid.

3. Results and discussion

3.1. Extraction behavior of M^{2+} in [Rmim][PF_6] systems

The extracted ratios (%E) of M^{2+} into extract phase ([bmim][PF_6], [hmim][PF_6], [omim][PF_6], nitrobenzene, chloroform and toluene) with Htta were plotted as a function of the aqueous phase pH in Fig. 2. The %E values, calculated from each metal concentration in back-extracted solution,

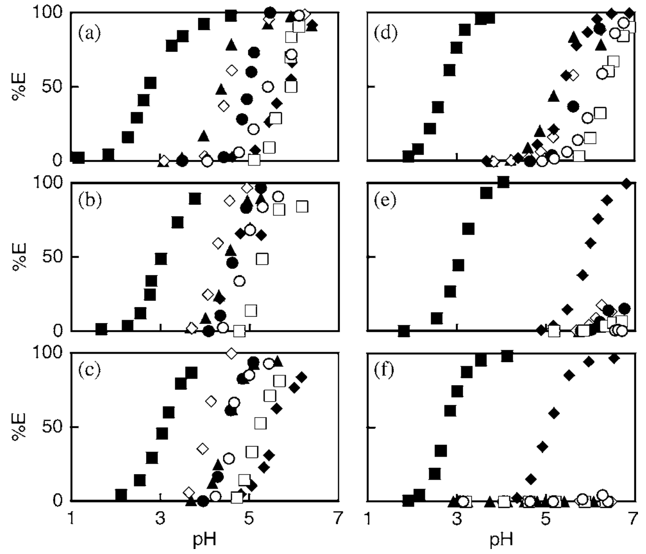

Fig. 2. Plots of the extracted ratios (%E) for some divalent metals as a function of the aqueous phase pH equilibrated with extraction phase in Htta system. Initial Htta concentration in extraction phase was $1 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$. Extraction phase: (a) [bmim][PF_6]; (b) [hmim][PF_6]; (c) [omim][PF_6]; (d) nitrobenzene; (e) chloroform; (f) toluene. Sample: (○), Mn^{2+}; (◇), Co^{2+}; (▲), Ni^{2+}; (■), Cu^{2+}; (●), Zn^{2+}; (□), Cd^{2+}; (◆), Pb^{2+}.

were compatible with the metal concentration remained in the equilibrated aqueous phase. (The sum of back-extracted metal amount and that remained in aqueous phase was usually more than 95% of its initial amount.) Namely, it was confirmed that the back-extraction using 1 mol dm^{-3} nitric acid is effective not only in conventional organic solvent systems but also in [Rmim][PF$_6$] systems.

As blank test, extraction experiment using Htta-free RTILs was performed at several aqueous phase pH condition. It was found that all of M^{2+} was not extracted in the absence of Htta in [Rmim][PF$_6$] systems. (Obtained %*E* was <2% (obviously less than experimental error) and M^{2+} amount remained in aqueous phase was >97% in all experimental condition.) From this result, it was found that Rmim$^+$ cations and PF$_6$$^-$ anion do not act as strong extractant in this system.

All of the RTILs showed much higher extraction ability than nitrobenzene, chloroform and toluene, except for M = Cu and Pb. Namely, it was found that the [Rmim][PF$_6$]-type hydrophobic RTILs can be used as chelate extraction solvents.

Obtained extraction selectivity order was $\mathrm{Cu} \gg \mathrm{Ni} \geq \mathrm{Co} > \mathrm{Zn} > \mathrm{Mn} > \mathrm{Pb} \approx \mathrm{Cd}$ for [bmim][PF$_6$], $\mathrm{Cu} \gg \mathrm{Co} > \mathrm{Pb} \approx \mathrm{Ni} \approx \mathrm{Zn} > \mathrm{Mn} > \mathrm{Cd}$ for [hmim][PF$_6$] and $\mathrm{Cu} > \mathrm{Co} > \mathrm{Ni} \approx \mathrm{Zn} \geq \mathrm{Mn} > \mathrm{Cd} > \mathrm{Pb}$ for [omim][PF$_6$]. It is remarkable that the selectivity order Co > Zn > Mn > Cd is kept in all RTIL systems.

3.2. Determination of the extracted species

Since RTIL phase has large amounts of exchangeable ionic species, M^{2+} can be extracted into the RTIL phase not only as neutral complex but also as cationic or anionic species. When M^{2+} forms complex with *m* Htta molecules and is extracted with release of *n* protons, the following extraction equilibria can be considered:

(i) cationic species ($n < 2$):

$$\mathrm{M}^{2+} + m\mathrm{Htta}_{(e)} + (2-n)\mathrm{Rmim}_{(e)}{}^{+} \rightleftharpoons \mathrm{M(tta)}_n(\mathrm{Htta})^{(2-n)+}_{m-n(e)} + n\mathrm{H}^+ + (2-n)\mathrm{Rmim}^+ \quad (1)$$

(ii) neutral species ($n = 2$):

$$\mathrm{M}^{2+} + m\mathrm{Htta}_{(e)} \rightleftharpoons \mathrm{M(tta)}_n(\mathrm{Htta})_{m-n(e)} + n\mathrm{H}^+ \quad (2)$$

(iii) anionic species ($n > 2$):

$$\mathrm{M}^{2+} + m\mathrm{Htta}_{(e)} + (n-2)\mathrm{PF}_{6(e)}{}^{-} \rightleftharpoons \mathrm{M(tta)}_n(\mathrm{Htta})^{(n-2)-}_{m-n(e)} + n\mathrm{H}^+ + (n-2)\mathrm{PF}_6{}^- \quad (3)$$

where subscript (e) shows extraction phase.

To determine *m* and *n* values, relationship between logarithmic distribution ratio of each metal (log *D*) and equilibrated pH at a fixed Htta concentration and that between log *D* versus Htta concentration at a fixed pH were studied. The slopes of these plots show *m* and *n* values, respectively. Fig. 3 shows typical examples of these plots. In all of [bmim][PF$_6$], [hmim][PF$_6$] and [omim][PF$_6$] systems, $m = n = 2$ for M = Ni, Cu and Pb (ex. Fig. 3(a and c)) and $m = n = 3$ for M = Mn, Co, Zn and Cd (ex. Fig. 3(b and d)) were obtained. Namely, extraction equilibrium and extraction constant (K_{ex}) for M = Ni, Cu and Pb can be expressed as follows:

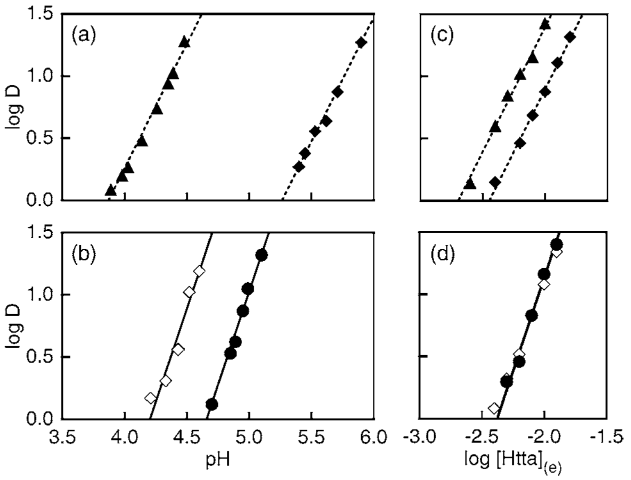

Fig. 3. Plots of the logarithmic distribution ratios (log *D*) for some divalent metals as a function of the aqueous phase pH (a and b) and those as that of logarithmic concentration of Htta in extraction phase (c and d). Initial Htta concentration in extraction phase was 1×10^{-2} mol dm^{-3} on (a) and (b), and pH was 4.3 (Ni^{2+}) and 5.6 (Pb^{2+}) on (c) and 4.5 (Co^{2+}) and 4.9 (Zn^{2+}) on (d). The broken line and solid line, of which the slope is 2 and 3, respectively, were obtained by the least squares fitting. Sample: (▲), Ni^{2+}; (◆), Pb^{2+}; (◇), Co^{2+}; (●), Zn^{2+}.

$$\mathrm{M}^{2+} + 2\mathrm{Htta}_{(e)} \rightleftharpoons \mathrm{M(tta)}_{2(e)} + 2\mathrm{H}^+ \quad (4)$$

$$K_{\mathrm{ex}} = \frac{[\mathrm{M(tta)}_2]_{(e)}[\mathrm{H}^+]^2}{[\mathrm{M}^{2+}][\mathrm{Htta}]_{(e)}{}^2} \quad (5)$$

and those for M = Mn, Co, Zn and Cd can be expressed as follows:

$$\mathrm{M}^{2+} + 3\mathrm{Htta}_{(e)} + \mathrm{PF}_{6(e)}{}^{-} \rightleftharpoons \mathrm{M(tta)}_{3(e)}{}^{-} + 3\mathrm{H}^+ + \mathrm{PF}_6{}^- \quad (6)$$

$$K_{\mathrm{ex}} = \frac{[\mathrm{M(tta)}_3{}^-]_{(e)}[\mathrm{H}^+]^3[\mathrm{PF}_6{}^-]}{[\mathrm{M}^{2+}][\mathrm{Htta}]^3_{(e)}[\mathrm{PF}_6{}^-]_{(e)}} \quad (7)$$

In the latter case, the [PF$_6$$^-$]$_{(e)}$ and [PF$_6$$^-$] values can be obviously regarded as constant ones (the aqueous phase is saturated with [Rmim][PF$_6$] salt), and the following value:

$$K_{\mathrm{ex}}{}' = \frac{K_{\mathrm{ex}}[\mathrm{PF}_6{}^-]_{(e)}}{[\mathrm{PF}_6{}^-]} = \frac{[\mathrm{M(tta)}_3{}^-]_{(e)}[\mathrm{H}^+]^3}{[\mathrm{M}^{2+}][\mathrm{Htta}]^3_{(e)}} \quad (8)$$

can be regarded as constant. Therefore, the log K_{ex} values for M = Ni, Cu and Pb and the log $K_{\mathrm{ex}}{}'$ values for M = Mn, Co, Zn and Cd can be calculated using extraction data as follows:

$$\log K_{\mathrm{ex}} = \log D - 2\mathrm{pH} - 2\log[\mathrm{Htta}]_{(e)} \quad (\mathrm{M} = \mathrm{Ni, Cu\ and\ Pb}) \quad (9)$$

Table 1
Determined $\log K_{ex}$ and $\log K_{ex}'$ values for divalent metal cations in $[Rmim][PF_6]$ systems (25 ± 1 °C)

Cation	Extraction phase		
	$[bmim][PF_6]$	$[hmim][PF_6]$	$[omim][PF_6]$
$\log K_{ex}$			
Ni^{2+}	-3.95 ± 0.11	-4.35 ± 0.06	-4.37 ± 0.09
Cu^{2+}	-0.62 ± 0.07	-1.31 ± 0.10	-1.44 ± 0.11
Pb^{2+}	-6.77 ± 0.11	-4.24 ± 0.15	-6.37 ± 0.12
$\log K_{ex}'$			
Mn^{2+}	-9.14 ± 0.08	-7.92 ± 0.05	-7.20 ± 0.27
Co^{2+}	-6.95 ± 0.11	-6.00 ± 0.05	-5.62 ± 0.22
Zn^{2+}	-8.19 ± 0.10	-7.14 ± 0.11	-6.83 ± 0.05
Cd^{2+}	-10.50 ± 0.08	-9.10 ± 0.06	-8.86 ± 0.16

$$\log K_{ex}' = \log D - 3\text{pH} - 3\log[\text{Htta}]_{(e)} \quad (\text{M} = \text{Mn, Co, Zn and Cd}) \qquad (10)$$

The obtained $\log K_{ex}$ and $\log K_{ex}'$ values were shown in Table 1.

In addition, it was confirmed that all of extracted species in nitrobenzene, chloroform and toluene systems were neutral $M(tta)_2$ as usual chelate extraction manner using HTTA [1,36–42]. Table 2 shows the obtained $\log K_{ex}$ values with those reported previously [1,36–42].

3.3. Extraction mechanism

As shown in Table 1, it is very interesting that the order of $\log K_{ex}$ value for M = Ni and Cu is $[bmim][PF_6] > [hmim][PF_6] > [omim][PF_6]$, whereas that of $\log K_{ex}'$ for M = Mn, Co, Zn and Cd is $[bmim][PF_6] < [hmim][PF_6] < [omim][PF_6]$. In other words, $M(tta)_2$ species seems to favor hydrophilic nature, whereas $M(tta)_3^-$ seems to favor hydrophobic one. These results provide us with very important information to suggest extraction mechanism in $[Rmim][PF_6]$ systems. (Unfortunately, we have no information to interpret the extraordinary result for M = Pb).

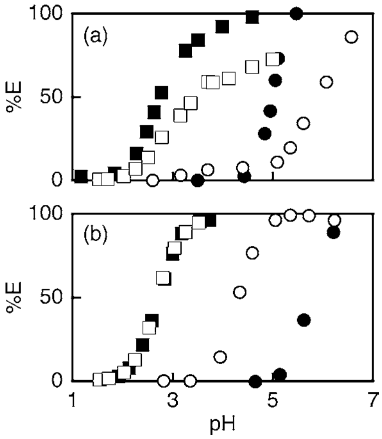

Fig. 4. Plots of the %*E* for some divalent metals as a function of the aqueous phase pH in Htta-TOPO (□, ○) and Htta alone (■, ●) systems. Initial concentration of Htta and TOPO (if co-existed) in extraction phase was 1×10^{-2} mol dm^{-3}. Extraction phase: (a) $[bmim][PF_6]$; (b) nitrobenzene. Sample: (□ ■), Cu^{2+}; (○ ●), Zn^{2+}.

In conventional chelate extraction using an organic solvent as extraction phase, further hydration to formed chelate often causes its low extractability. As shown in Fig. 2, in actual, divalent metal cations except for Cu^{2+} and Pb^{2+} were hardly extracted into chloroform or toluene. To evaluate the effect of hydration in the $[Rmim][PF_6]$-Htta extraction systems, synergistic extraction of the divalent metals using Htta and tri-*n*-octylphosphine oxide (TOPO) was performed. TOPO is neutral monodentate ligand having strong coordination ability and hydrophobicity and, therefore, is exchangeable with hydrated water and, sometimes, other coordinating ligand in extracted complex. Fig. 4 shows typical examples of comparison between extraction behavior in Htta-TOPO system and that in Htta alone system. In $[Rmim][PF_6]$ systems, co-existence of TOPO resulted in lowering in extraction performance on the contrary in conventional systems. In the

Table 2
Determined and reported $\log K_{ex}$ values for divalent metal cations in nitrobenzene, chloroform, toluene, benzene and carbon tetrachloride systems (25 ± 1 °C)

Cation	Extraction phase				
	Nitrobenzene	Chloroform	Toluene	Benzene	Carbon tetrachlorode
Mn^{2+}	-7.60 ± 0.07	N.D.[a] -10.83 [36]	N.D.	-10.07 [36]	-11.34 [36]
Co^{2+}	-6.30 ± 0.05	N.D. -8.63 [37]	N.D. -8.62 [37]	-6.70 [1]	-8.96 [41]
Ni^{2+}	-5.60 ± 0.11	N.D.	N.D.	-6.6 [40]	
Cu^{2+}	-0.73 ± 0.06	-1.47 ± 0.06 -1.25 [38]	-0.84 ± 0.05	-1.32 [1]	-1.08 [38]
Zn^{2+}	-6.66 ± 0.11	N.D. -8.13 [38]	N.D. -8.0 [39]	-7.9 [39]	-8.04 [38]
Cd^{2+}	-7.95 ± 0.05	N.D.	N.D.		
Pb^{2+}	-6.11 ± 0.05	-7.13 ± 0.07	-5.36 ± 0.05	-5.24 [1]	-10.60 [42]

[a] Not determined because of low extractability.

Htta-TOPO system, furthermore, the sum of back-extracted metal amount and that remained in aqueous phase was suppressed with the increase of aqueous phase pH, which suggests formation of insoluble species containing M^{2+} and TOPO. From this result and above-mentioned facts, the following extraction mechanism in the RTIL systems was suggested.

For M = Cu and Ni (and probably Pb), extracted species in $[Rmim][PF_6]$ phase seems to be hydrated $M(tta)_2(H_2O)$ or $M(tta)_2(H_2O)_2$. Although Cu(II) and Ni(II) can form square-planer complex in which the coordination number of the metal is four, in high polar RTIL phase, the hydrated complex having larger coordination number seems to be more stable. It is well known that solubility of water in $[Rmim][PF_6]$-type RTILs is very large and is decreased with the increase of 1-alkyl chain length in $Rmim^+$ [43]. In actual, the value for $[bmim][PF_6]$ was reported as 2.3 ± 0.2 wt.% whereas that for $[omim][PF_6]$ was 1.3 ± 0.5 wt.% [44]. The solubility order is the same as that of $\log K_{ex}$. In the proposed mechanism, decrease of the extractability by adding TOPO can be interpreted as fall of affinity to $[Rmim][PF_6]$ media by ligand-exchange reaction between hydrated water and TOPO. In addition, the competitively formed adducts, probably $M(tta)_2(TOPO)$ or $M(tta)_2(TOPO)_2$, seemed to be precipitated.

$M(tta)_3^-$ (M = Mn, Co, Zn and Cd) is coordination-saturated hydrophobic and anionic complex and, in $[Rmim][PF_6]$ phase, is stabilized by electrostatic interaction with $Rmim^+$. This stabilization seems to be more effective in the use of more hydrophobic cation because of its ion-pair formation tendency. The order of hydrophobicity is $bmim^+ < hmim^+ < omim^+$, which is the same as that of $\log K_{ex}'$ in $[Rmim][PF_6]$ systems. Furthermore, this interaction does not contribute extraction selectivity, resulting in the invariable $\log K_{ex}'$ order, Co > Zn > Mn > Cd. In this mechanism, decrease of the extractability by adding TOPO can be interpreted as loss of anionic charge in the extracted species by ligand-exchange reaction between anionic tta^- and neutral TOPO. In addition, the competitively formed adducts, probably $M(tta)_2(TOPO)(H_2O)$ or $M(tta)_2(TOPO)_2$, seemed to be precipitated.

As mentioned above, two different extraction mechanisms acted in the RTIL extraction systems. Although co-existence of the two mechanisms seems to be not only for $[Rmim][PF_6]$-Htta systems but also for other RTIL-bidentate monoanionic extractant systems, superiority between the mechanisms may be controlled by many factors. In other words, chelate extraction using RTILs has possibility to realize novel extractive separation by tuning extraction system.

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