Distribution Equilibria of Amphoteric 8-Quinolinol between 1-Alkyl-3-methylimidazolium Bis(trifluoromethanesulfonyl)imide and Aqueous Phases and Their Effect on Ionic Liquid Chelate Extraction Behavior of Iron(III)

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The distribution behavior of amphoteric 8-quinolinol (HQ) between ionic liquid (IL) phase and aqueous phase and ionic liquid chelate extraction behavior of iron(III) with HQ were investigated using four 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($C_n\text{mimTf}_2\text{N}$, $n = 2, 4, 6$ and 8) ILs. Not only neutral HQ but also cationic H_2Q^+ were distributed into the IL phase, and the latter distribution based on cation-exchange with $C_n\text{mim}^+$ was pronounced in the use of IL having a less-hydrophobic cation, such as C_2mim^+ . In the IL chelate extraction of iron(III), the extractability increased with the increase in the hydrophobicity of IL as the extraction phase. Nevertheless, the determined equilibrium constants for the extraction as the neutral complex FeQ_3 were similar to one another. The difference in the extractability among the ILs was due to the difference in the distribution of H_2Q^+ into the extraction phase. In addition, the cationic coordinatively-unsaturated complex FeQ_2^+ was also extracted in use of less-hydrophobic $\text{C}_2\text{mimTf}_2\text{N}$.

Keywords Ionic liquids, 8-quinolinol, cation-exchange, chelate extraction, iron(III)

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Introduction

Ionic liquids (ILs) are generally defined as “liquids composed entirely of ions that are fluid around or below 100°C ”,¹ which have attracted much attention as novel liquid media. ILs are also used in analytical chemistry, including electroanalytical chemistry^{2,3} and separation chemistry.⁴⁻⁷

Solvent extraction of metal cations is a separation technique using large amounts of hydrophobic organic solvents for the extraction phase materials. Therefore, possible use of hydrophobic ILs, including 1-alkyl-3-methylimidazolium hexafluorophosphate ($C_n\text{mimPF}_6$) and 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($C_n\text{mimTf}_2\text{N}$), as alternatives to the organic solvents has been energetically investigated.⁸⁻¹⁹ Among several approaches, ionic liquid chelate extraction using Brønsted acidic chelators as extraction reagents^{20,21} is interesting because a change in the aqueous-phase pH results in changing the extraction performance.

In conventional chelate extraction process using organic solvents, metal cations are generally extracted as neutral complexes. Although hydrophobic ILs have relatively high polarity,²² many kinds of metal cations are extracted as neutral complexes in IL chelate extraction as well. However, hydrophobic ILs also have ion-exchange abilities²³ and, therefore, charged complexes may be extracted. For example, several divalent transition metals^{20,24} and trivalent lanthanoids²⁵ were extracted into ILs with 2-thenoyltrifluoroacetone (Htta) as

monoanionic complexes. Moreover, the ion-exchange abilities may affect the distribution behavior of extraction reagents between the two phases. Actually, anionic tta^- showed a quite high affinity to the IL phase.²⁶

8-Hydroxyquinoline (HQ) is a well-known bidentate extraction reagent. Although there are many papers on use of HQ in IL chelate extraction,²⁷⁻³⁷ the distribution behavior of HQ between IL and aqueous phases has not been investigated. HQ is an amphoteric compound, which has the following two acid-base equilibria:

The formation of cationic H_2Q^+ in the aqueous phase causes suppression of the chelate extraction as a side reaction; also, the distribution of the cationic H_2Q^+ into the IL phase can result in a further enhancement of the suppression. Namely, evaluating the distribution behavior of HQ between the phases is very important for investigating the IL chelate extraction behavior of metals with HQ, particularly in the acidic condition. In this study, the distribution behavior of HQ into several 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($C_n\text{mimTf}_2\text{N}$) ILs was evaluated, and its effect on the IL chelate extraction behavior of iron(III) was investigated.

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Experimental

Chemicals

Four ILs [1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($C_2\text{mimTf}_2\text{N}$), 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($C_4\text{mimTf}_2\text{N}$), 1-hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($C_6\text{mimTf}_2\text{N}$) and 1-methyl-3-octylimidazolium bis(trifluoromethanesulfonyl)imide ($C_8\text{mimTf}_2\text{N}$)] were synthesized according to a reported procedure.^{38,39} The extraction reagent HQ was purchased from Wako Pure Chemical Industries (Osaka, Japan). Other chemicals and solvents included reagent-grade materials, which were used without further purification. High-purity water was produced with a Millipore Direct-Q water-purification system.

Apparatus

The absorption spectra of solutions were recorded on a JASCO V-630 UV/visible spectrophotometer using 1 cm matched quartz cells. A Thermo Fischer Scientific iCE3000 flame atomic absorption spectrophotometer was used for determining of the concentration of a metal in the aqueous phase. A Horiba Model F-52 pH meter equipped with a Horiba 9680S-10D combined glass electrode was used to determine the pH values.

Distribution of HQ

The distribution of the extraction reagent between $C_n\text{mimTf}_2\text{N}$ and aqueous phases was measured as follows. In a centrifuge tube, an aliquot (8.0 cm^3) of aqueous solution containing $5.0 \times 10^{-4}\text{ mol dm}^{-3}$ HQ, $1 \times 10^{-1}\text{ mol dm}^{-3}$ sodium chloride and $1 \times 10^{-2}\text{ mol dm}^{-3}$ of buffer [chloroacetic acid, acetic acid, 2-(*N*-morpholino)ethanesulfonic acid, 3-(*N*-morpholino)propanesulfonic acid, *N*-tris(hydroxymethyl)methyl-3-aminopropanesulfonic acid or *N*-cyclohexyl-2-aminoethanesulfonic acid] or suitable concentration of hydrochloric acid or sodium hydroxide was shaken with 1.0 cm^3 of $C_n\text{mimTf}_2\text{N}$ at $25 \pm 1^\circ\text{C}$ for 30 min to be equilibrated. After the two phases were separated by centrifugation, the pH in the aqueous phase was determined and the measured pH was used as the equilibrated pH. The equilibrated aqueous phase was diluted by using 1 mol dm^{-3} NaOH, after which absorbance of the diluted solution at 353.5 nm (maximum absorption wavelength for Q^-) was measured to determine the HQ concentration in the aqueous phase. Its concentration in the $C_n\text{mimTf}_2\text{N}$ phase was calculated from the mass balance, and the distribution ratio of HQ (D_{HQ}) was calculated using these values. In addition, the distribution of NaCl and the buffer components into the IL phase was regarded as being negligible.

Distribution of Fe(III)

The distribution of Fe(III) between $C_n\text{mimTf}_2\text{N}$ and aqueous phases in the IL chelate extraction system was measured as follows. In a centrifuge tube, an aliquot (1.0 cm^3) of a $C_n\text{mimTf}_2\text{N}$ phase containing $1.0 \times 10^{-2}\text{ mol dm}^{-3}$ of HQ and 5.0 cm^3 of an aqueous phase containing $3.4 \times 10^{-5}\text{ mol dm}^{-3}$ (2.0 mg dm^{-3}) of Fe(III), $1.0 \times 10^{-1}\text{ mol dm}^{-3}$ of potassium nitrate and $1.0 \times 10^{-2}\text{ mol dm}^{-3}$ of buffer (chloroacetic acid or acetic acid) were shaken mechanically at $25 \pm 1^\circ\text{C}$ for 30 min to be equilibrated. After the two phases were separated by centrifugation, the pH in the aqueous phase was determined. The Fe concentration in the aqueous phase and that in the organic phase (after back-extraction into 1.0 mol dm^{-3} nitric acid) were determined by flame AAS. The extractability (%*E*) and the distribution ratio (*D*) of Fe were calculated with using

Fig. 1 Relationship between logarithmic the distribution ratio of HQ ($\log D_{\text{HQ}}$) and the aqueous phase pH. The solid curves were obtained by a non-linear least squares fitting. Extraction phase: (a) $C_2\text{mimTf}_2\text{N}$; (b) $C_4\text{mimTf}_2\text{N}$; (c) $C_6\text{mimTf}_2\text{N}$; (d) $C_8\text{mimTf}_2\text{N}$.

these values. In addition, distribution of KNO_3 and the buffer components into the IL phase was regarded as being negligible.

Results and Discussion

Distribution equilibria of HQ

The pH dependency in the distribution of HQ between IL and aqueous phases was investigated at the pH range of 1 – 12 with using the four ILs. Figure 1 shows the relationship between $\log D_{\text{HQ}}$ and the aqueous phase pH for the four systems. In all systems, $\log D_{\text{HQ}}$ showed a constant value not only at neutral pH (*ca.* 6 – 8) but also at acidic pH (*ca.* 1 – 2). This result indicated that not only neutral HQ but also cationic H_2Q^+ distribute in the IL phases. In addition, the distribution of anionic Q^- was negligibly low in this study.

The distribution equilibrium of neutral HQ is

where subscript IL shows the IL phase, and the distribution constant, $K_{\text{D,HQ}}$ is defined as

$$K_{\text{D,HQ}} = [\text{HQ}]_{\text{IL}}/[\text{HQ}]. \quad (4)$$

The distribution equilibrium of acidic H_2Q^+ , on the contrary, is based on the cation-exchange reaction shown as

Table 1 Obtained $\log K_{D,HQ}$, $\log K'_{D,H2Q+}$ and $\log K_{D,H2Q+}$ values

Extraction solvent	$\log K_{D,HQ}$	$\log K'_{D,H2Q+}$	$K_{SP}/\text{mol}^2 \text{ dm}^{-6.40}$	$\log K_{D,H2Q+}$
C ₂ mimTf ₂ N	1.90 ± 0.01	1.36 ± 0.01	2.17×10^{-3}	0.03
C ₄ mimTf ₂ N	2.05 ± 0.01	0.87 ± 0.01	2.91×10^{-4}	-0.89
C ₆ mimTf ₂ N	2.16 ± 0.01	0.32 ± 0.01	2.82×10^{-5}	-1.96
C ₈ mimTf ₂ N	2.16 ± 0.01	-0.28 ± 0.02	3.49×10^{-6}	-3.01

Also the equilibrium constant, $K_{D,H2Q+}$, can be defined as

$$K_{D,H2Q+} = [\text{H}_2\text{Q}^+]_{\text{IL}}[\text{C}_n\text{mim}^+]/[\text{H}_2\text{Q}^+]. \quad (6)$$

(The activity of C_nmim^+ in the IL phase is defined as unity.) Since the total amount of HQ is sufficiently small compared with C_nmim^+ , $[\text{C}_n\text{mim}^+]$ can be approximately calculated from the solubility product of $\text{C}_n\text{mimTf}_2\text{N}$ (K_{SP}) as follows:

$$[\text{C}_n\text{mim}^+] = [\text{Tf}_2\text{N}^-] = K_{SP}^{1/2}, \quad (7)$$

and the following apparent distribution constant, $K'_{D,H2Q+}$, can be defined:

$$\begin{aligned} K'_{D,H2Q+} &= [\text{H}_2\text{Q}^+]_{\text{IL}}/[\text{H}_2\text{Q}^+] \\ &= K_{D,H2Q+}/[\text{C}_n\text{mim}^+] = K_{D,H2Q+}K_{SP}^{-1/2}. \end{aligned} \quad (8)$$

When using $K_{D,HQ}$ and $K'_{D,H2Q+}$, D_{HQ} is presented as a function of $[\text{H}^+]$, as follows:

$$\begin{aligned} D_{HQ} &= ([\text{H}_2\text{Q}^+]_{\text{IL}} + [\text{HQ}]_{\text{IL}})/([\text{H}_2\text{Q}^+] + [\text{HQ}] + [\text{Q}^-]) \\ &= (K'_{D,H2Q+}[\text{H}^+]K_{a1}^{-1} + K_{D,HQ})/([\text{H}^+]K_{a1}^{-1} + 1 + K_{a2}[\text{H}^+]^{-1}), \end{aligned} \quad (9)$$

where K_{a1} and K_{a2} are the acid dissociation constants of HQ for Eqs. (1) and (2), respectively.

Based on Eq. (9), the values of $\log K_{D,HQ}$ and $\log K'_{D,H2Q+}$ were calculated using a non-linear least-squares fitting to Fig. 1. The obtained values are summarized in Table 1 with $\log K_{D,H2Q+}$ calculated with using K_{SP} values.⁴⁰ In consideration with dissolution equilibrium for $\text{C}_n\text{mimTf}_2\text{N}$, possible deviation of actual $[\text{C}_n\text{mim}^+]$ from $K_{SP}^{1/2}$ was numerically estimated as being within 1% (0.005 logarithmic unit), and it was confirmed that the approximation shown in Eq. (7) is appropriate in this case. In addition, the $\text{p}K_{a1}$ and $\text{p}K_{a2}$ values for HQ were also calculated from the data as 5.12 ± 0.04 and 9.93 ± 0.07 , respectively. These values are close to ones reported previously (5.00 and 9.66, respectively⁴¹).

Although similar $\log K_{D,HQ}$ values were obtained for all systems, more hydrophobic IL showed a marginally larger $\log K_{D,HQ}$ value. This tendency is similar to the case of Htta.²⁶ On the contrary, the $\log K'_{D,H2Q+}$ (and $\log K_{D,H2Q+}$) values were quite different between the systems. Being concrete, the order of $\log K'_{D,H2Q+}$ value was $\text{C}_2\text{mimTf}_2\text{N} > \text{C}_4\text{mimTf}_2\text{N} > \text{C}_6\text{mimTf}_2\text{N} > \text{C}_8\text{mimTf}_2\text{N}$ and IL having a more hydrophobic cation showed a lower $\log K'_{D,H2Q+}$ value. This order is the same as the distribution of various cations, including 1-ethylpyridinium.⁴²

Extraction of Fe(III) with HQ

For the four IL extraction systems, the %E values of Fe(III) were plotted as a function of the aqueous phase pH. The results are shown in Fig. 2. For a comparison, those using conventional organic solvents, such as toluene and chloroform, are also plotted in the figure. Interestingly, there is an obvious difference in the extractability among the four systems. The extractability

Fig. 2 Plots of the extractability of Fe(III) (%E) as a function of the aqueous phase pH. Initial HQ concentration in the extraction phase was $1.0 \times 10^{-2} \text{ mol dm}^{-3}$. Extraction phase: ○, C₂mimTf₂N; ●, C₄mimTf₂N; ◇, C₆mimTf₂N; ◆, C₈mimTf₂N; □; toluene; ■, chloroform.

order was (chloroform >) $\text{C}_8\text{mimTf}_2\text{N} \approx \text{C}_6\text{mimTf}_2\text{N} > \text{C}_4\text{mimTf}_2\text{N} > \text{C}_2\text{mimTf}_2\text{N} (\approx \text{toluene})$.

In the chelate extraction of Fe(III) with HQ into a conventional organic solvent, Fe(III) is generally extracted as neutral complex FeQ_3 . In that into an IL, however, not only neutral FeQ_3 but also cationic complex such as FeQ_2^+ may be extracted as follows:

Also, the respective extraction constants are defined as follows:

$$K_{\text{ex,FeQ}_3} = [\text{FeQ}_3]_{\text{IL}}[\text{H}^+]^3/[\text{Fe}^{3+}][\text{HQ}]_{\text{IL}}^3, \quad (12)$$

$$K_{\text{ex,FeQ}_2^+} = [\text{FeQ}_2^+]_{\text{IL}}[\text{H}^+]^2[\text{C}_n\text{mim}^+]/[\text{Fe}^{3+}][\text{HQ}]_{\text{IL}}^2. \quad (13)$$

These constants can be represented as

$$K_{\text{ex,FeQ}_3} = K_{D,HQ}^{-3}K_{a2}^3\beta_{\text{FeQ}_3}K_{D,\text{FeQ}_3}, \quad (14)$$

$$K_{\text{ex,FeQ}_2^+} = K_{D,HQ}^{-2}K_{a2}^2\beta_{\text{FeQ}_2^+}K_{D,\text{FeQ}_2^+}, \quad (15)$$

where stability constants, β_{FeQ_3} and $\beta_{\text{FeQ}_2^+}$, are respectively defined as

$$\beta_{\text{FeQ}_3} = [\text{FeQ}_3]/[\text{Fe}^{3+}][\text{Q}^-]^3, \quad (16)$$

$$\beta_{\text{FeQ}_2^+} = [\text{FeQ}_2^+]/[\text{Fe}^{3+}][\text{Q}^-]^2, \quad (17)$$

and the distribution constants, K_{D,FeQ_3} and K_{D,FeQ_2^+} , are respectively defined as

$$K_{D,\text{FeQ}_3} = [\text{FeQ}_3]_{\text{IL}}/[\text{FeQ}_3], \quad (18)$$

$$K_{D,\text{FeQ}_2^+} = [\text{FeQ}_2^+]_{\text{IL}}[\text{C}_n\text{mim}^+]/[\text{FeQ}_2^+]. \quad (19)$$

In this case, the products $\beta_{\text{FeQ}_3}K_{D,\text{FeQ}_3}$ and $\beta_{\text{FeQ}_2^+}K_{D,\text{FeQ}_2^+}$ correspond to the equilibrium constants for the following reactions, respectively:

In addition, when using the following apparent distribution constant,

$$\begin{aligned} K'_{\text{D,FeQ}_2^+} &= [\text{FeQ}_2^+]_{\text{IL}}/[\text{FeQ}_2^+] \\ &= K_{\text{D,FeQ}_2^+}/[\text{C}_n\text{mim}^+] = K_{\text{D,FeQ}_2^+}K_{\text{SP}}^{-1/2}, \end{aligned} \quad (22)$$

the product $\beta_{\text{FeQ}_2^+}K'_{\text{D,FeQ}_2^+}$ can be used as the apparent equilibrium constant for Eq. (21).

With consideration for the above-mentioned complicated distribution equilibria for HQ, the extracted Fe(III) species in the IL chelate extraction system was determined from the relationship between D and $[\text{Q}^-]$. The $[\text{Q}^-]$ values were

Fig. 3 Plots of $\log D\alpha$ for Fe(III) as a function of $\log[\text{Q}^-]$. The initial HQ concentration in the extraction phase was $1.0 \times 10^{-2} \text{ mol dm}^{-3}$. The thick bold curve (a) was obtained by a non-linear least-squares fitting. (The fine solid line and the fine broken line are asymptotic ones with a slope of 2 and 3, respectively.) The thick broken lines (b – d) were obtained by a linear least-squares fitting with a slope of 3. Extraction phase: (a) $\text{C}_2\text{mimTf}_2\text{N}$; (b) $\text{C}_4\text{mimTf}_2\text{N}$; (c) $\text{C}_6\text{mimTf}_2\text{N}$; (d) $\text{C}_8\text{mimTf}_2\text{N}$.

calculated using the obtained distribution constants. In this case, possible deviation of $[\text{C}_n\text{mim}^+]$ from $K_{\text{SP}}^{1/2}$ was estimated as within 5% (0.02 logarithmic unit). Figure 3 shows relationship between $\log D\alpha$ for Fe(III) and $\log[\text{Q}^-]$, where the side reaction coefficient α (for hydrolysis of Fe(III)) is defined as

$$\begin{aligned} \alpha &= ([\text{Fe}^{3+}] + [\text{Fe}(\text{OH})^{2+}] + [\text{Fe}(\text{OH})_2^+] + [\text{Fe}(\text{OH})_3])/[\text{Fe}^{3+}] \\ &= 1 + \beta_{\text{Fe}(\text{OH})}[\text{OH}^-] + \beta_{\text{Fe}(\text{OH})_2}[\text{OH}^-]^2 + \beta_{\text{Fe}(\text{OH})_3}[\text{OH}^-]^3, \end{aligned} \quad (23)$$

and the stability constants of hydroxo complexes, $\beta_{\text{Fe}(\text{OH})}$, $\beta_{\text{Fe}(\text{OH})_2}$ and $\beta_{\text{Fe}(\text{OH})_3}$, are $10^{11.81}$, $10^{22.2}$ and 10^{30} , respectively.⁴³

When using $\text{C}_4\text{mimTf}_2\text{N}$, $\text{C}_6\text{mimTf}_2\text{N}$ and $\text{C}_8\text{mimTf}_2\text{N}$, the plots showed a straight line with a slope of *ca.* 3 (Figs. 3b – 3d). It was subsequently confirmed that Fe(III) is extracted into these phases as neutral FeQ_3 as shown Eq. (20). In these cases, $D\alpha$ is expressed as

$$D\alpha = [\text{FeQ}_3]_{\text{IL}}/[\text{Fe}^{3+}] = [\text{Q}^-]^3\beta_{\text{FeQ}_3}K_{\text{D,FeQ}_3}, \quad (24)$$

$$\begin{aligned} \log D\alpha &= \log([\text{FeQ}_3]_{\text{IL}}/[\text{Fe}^{3+}]) \\ &= 3\log[\text{Q}^-] + \log \beta_{\text{FeQ}_3}K_{\text{D,FeQ}_3}. \end{aligned} \quad (25)$$

Also, $\log \beta_{\text{FeQ}_3}K_{\text{D,FeQ}_3}$ can be obtained with using linear least squares fitting. When using $\text{C}_2\text{mimTf}_2\text{N}$, on the contrary, the plot showed a curve having two asymptotic lines with slopes of 2 and 3 (Fig. 3(a)), which suggested that neutral FeQ_3 and cationic FeQ_2^+ are competitively extracted into the $\text{C}_2\text{mimTf}_2\text{N}$ phase as shown in Eqs. (20) and (21). In this case, $D\alpha$ is shown as

$$\begin{aligned} D\alpha &= ([\text{FeQ}_3]_{\text{IL}} + [\text{FeQ}_2^+]_{\text{IL}})/[\text{Fe}^{3+}] \\ &= [\text{Q}^-]^3\beta_{\text{FeQ}_3}K_{\text{D,FeQ}_3} + [\text{Q}^-]^2\beta_{\text{FeQ}_2^+}K'_{\text{D,FeQ}_2^+}, \end{aligned} \quad (26)$$

and the two logarithmic constants, $\log \beta_{\text{FeQ}_3}K_{\text{D,FeQ}_3}$ and $\log \beta_{\text{FeQ}_2^+}K'_{\text{D,FeQ}_2^+}$ can be calculated with using non-linear least squares fitting to Fig. 3(a). The obtained values of $\log \beta_{\text{FeQ}_3}K_{\text{D,FeQ}_3}$ and $\log \beta_{\text{FeQ}_2^+}K'_{\text{D,FeQ}_2^+}$ and the calculated values of $\log K_{\text{ex,FeQ}_3}$, $\log \beta_{\text{FeQ}_2^+}K_{\text{D,FeQ}_2^+}$ and $\log K_{\text{ex,FeQ}_2^+}$ are summarized in Table 2.

Although these four IL extraction systems showed obviously different extractability for Fe(III), the obtained $\log \beta_{\text{FeQ}_3}K_{\text{D,FeQ}_3}$ and $\log K_{\text{ex,FeQ}_3}$ values are very similar to one another. From these facts, we focused attention on the cation-exchange distribution of protonated H_2Q^+ into the IL phase shown as Eq. (5). Namely, a large distribution of H_2Q^+ is followed by the large decrease in the concentration of HQ in the IL phase and that of Q^- in the aqueous phase. The values of $[\text{H}_2\text{Q}^+]_{\text{IL}}$, $[\text{HQ}]_{\text{IL}}$ and $[\text{Q}^-]$ at pH 2.0 calculated from the determined equilibrium constants for HQ are given in Table 3 as example. The $[\text{HQ}]_{\text{IL}}$ in the $\text{C}_2\text{mimTf}_2\text{N}$ system having high $\log K'_{\text{D,H}_2\text{Q}^+}$ was *ca.* 9-fold lower than that in the $\text{C}_8\text{mimTf}_2\text{N}$ system having low one, and the $[\text{Q}^-]$ was *ca.* 5-fold lower. It was confirmed that the cation-exchange distribution of H_2Q^+ acts as a competitive side-reaction to control the extraction performance for Fe(III).

The competitive extraction of cationic FeQ_2^+ was confirmed only concerning the use of less-hydrophobic $\text{C}_2\text{mimTf}_2\text{N}$ as the

Table 2 Obtained $\log \beta_{\text{FeQ}_3}K_{\text{D,FeQ}_3}$, $\log K_{\text{ex,FeQ}_3}$, $\log \beta_{\text{FeQ}_2^+}K'_{\text{D,FeQ}_2^+}$, $\log \beta_{\text{FeQ}_2^+}K_{\text{D,FeQ}_2^+}$ and $\log K_{\text{ex,FeQ}_2^+}$ values

Extraction solvent	$\log \beta_{\text{FeQ}_3}K_{\text{D,FeQ}_3}$	$\log K_{\text{ex,FeQ}_3}$	$\log \beta_{\text{FeQ}_2^+}K'_{\text{D,FeQ}_2^+}$	$\log \beta_{\text{FeQ}_2^+}K_{\text{D,FeQ}_2^+}$	$\log K_{\text{ex,FeQ}_2^+}$
$\text{C}_2\text{mimTf}_2\text{N}$	40.97 ± 0.07	5.47	27.83 ± 0.05	26.50	2.83
$\text{C}_4\text{mimTf}_2\text{N}$	41.68 ± 0.04	5.74	—	—	—
$\text{C}_6\text{mimTf}_2\text{N}$	41.84 ± 0.01	5.56	—	—	—
$\text{C}_8\text{mimTf}_2\text{N}$	41.54 ± 0.03	5.25	—	—	—

Table 3 Calculated values of $[H_2Q^+]_{IL}$, $[HQ]_{IL}$ and $[Q^-]$ at pH 2.0

Extraction solvent	$[H_2Q^+]_{IL}/\text{mol dm}^{-3}$	$[HQ]_{IL}/\text{mol dm}^{-3}$	$[Q^-]/\text{mol dm}^{-3}$
C ₂ mimTf ₂ N	8.21×10^{-3}	2.15×10^{-5}	3.16×10^{-15}
C ₄ mimTf ₂ N	5.96×10^{-3}	6.76×10^{-5}	7.08×10^{-15}
C ₆ mimTf ₂ N	2.89×10^{-3}	1.53×10^{-4}	1.24×10^{-14}
C ₈ mimTf ₂ N	9.26×10^{-4}	1.97×10^{-4}	1.58×10^{-14}

Initial HQ concentration in the IL phase: $1.0 \times 10^{-2} \text{ mol dm}^{-3}$.

extraction phase. The specific behavior seems to originate in its relatively low extractability for neutral FeQ₃, as mentioned above, and in its relatively high ability in cation-exchange extraction based on the low hydrophobicity of C₂mim⁺. In addition, FeQ₂⁺ is a coordinatively-unsaturated complex and, therefore, is hydrated in the aqueous phase. Namely, it was suggested that coordinatively-unsaturated chelates can be extracted in IL chelate extraction under a suitable condition.

Conclusion

First, the distribution behavior of HQ between IL and aqueous phases was investigated with using the four ILs having different hydrophobicity. Not only neutral HQ but also cationic H₂Q⁺ were distributed into the IL phase. A similar distribution behavior for the HQ was shown for all ILs, whereas a different distribution behavior for the H₂Q⁺ based on cation-exchange was observed among the ILs with the order of C₂mimTf₂N > C₄mimTf₂N > C₆mimTf₂N > C₈mimTf₂N and the order is same as that in conventional cation-exchange extraction in IL system.

In the IL chelate extraction of Fe(III) with HQ, the extractability order was C₈mimTf₂N ≈ C₆mimTf₂N > C₄mimTf₂N > C₂mimTf₂N. Since the determined equilibrium constants for the extraction as neutral complex FeQ₃ were similar among the four extraction systems, it was found that the difference in the Fe(III)-extractability is due to that in distribution of H₂Q⁺. In the use of C₂mimTf₂N having low-hydrophobic C₂mim⁺, moreover, cationic FeQ₂⁺ was competitively extracted. In conclusion, it was found that the distribution of amphoteric extraction reagents can affect its IL chelate extraction performance.

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