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COMMUNICATION

Extraction of Pd(II), Rh(III) and Ru(III) from HNO$_3$ aqueous solution to betainium bis(trifluoromethanesulfonyl)imide ionic liquid

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Extraction efficiencies of Pd(II), Rh(III), and Ru(III) from HNO$_3$(aq) to [Hbet][Tf$_2$N] were demonstrated, *i.e.*, Pd(II) is most extractable, Rh(III) is the middle, and Ru(III) is the least. The extraction seems to proceed through coordination of betaine to the metal ions and the cation exchange of the formed complex with H$^+$.

Ionic liquids (ILs) consist of only ionic species, and have unique properties, *e.g.*, low melting points despite salts, very low volatility, high conductivity, and wide electrochemical window. Especially, the vapour pressures of ILs are practically negligible.[1] Therefore ILs are expected to be applicable as non-aqueous media in solvent extraction processes instead of conventional organic solvents.[2]

A betainium cation (Me$_3$N$^+$CH$_2$COOH, [Hbet]$^+$) is prepared by trimethylation of N in glycine, and its combination with a bis(trifluoromethanesulfonyl)imide anion ([Tf$_2$N]$^-$) forms an IL, [Hbet][Tf$_2$N].[3] This IL shows an additional thermomorphic behaviour that it is immiscible with aqueous phase at ambient temperature, while they become homogeneous with heating. The upper critical solution temperature (UCST) of the [Hbet][Tf$_2$N]-water mixture is 55°C. This unique behaviour of [Hbet][Tf$_2$N] is intended to be applied to accelerate the extraction process. Furthermore, the cation component [Hbet]$^+$ is functionalized by a carboxylic group, which may have coordination affinity with various metal ions (M^{n+}). Therefore, an "extractant-less" extraction method would be expected to be established by using this task-specific IL.

Recently, Hoogerstraete *et al.* tested the efficiency of [Hbet][Tf$_2$N] to extract various minor metal ions such as rare earths, indium, gallium, and several transition metals. In this experiment a zwitterionic betaine (Me$_3$N$^+$CH$_2$COO$^-$, bet) was present as an additive in the actual system to facilitate the extraction.[3c] In addition, this research group just dissolved Tf$_2$N$^-$ salts of the studied M^{n+} in water to avoid the anion exchange. Although this is preferable to clarify fundamentals of the extraction chemistry, it is also important to consider the foregoing process to dissolve metals of interest. An oxidizing acid like HNO$_3$ is frequently used for this purpose. Therefore, it is mandatory to clarify the extraction behaviour of M^{n+} in the [Hbet][Tf$_2$N]-HNO$_3$(aq) biphasic system in order to come

closer to industrial applications. In this study, we selected Pd(II), Rh(III), and Ru(III) as M^{n+} of interest, because these are comprised in the platinum group metals or *platinoids* of which recovery from metal stocks in society[4] and spent nuclear fuels[5] is demanded. Herein, we report the extraction behaviour of Pd(II), Rh(III), and Ru(III) from HNO$_3$(aq) to [Hbet][Tf$_2$N], and assess the possibility of efficient mutual separation of these elements in the [Hbet][Tf$_2$N]-HNO$_3$(aq) system.

The dried [Hbet][Tf$_2$N] is a solid at room temperature, whereas it forms a viscous liquid by saturation of water. [Hbet][Tf$_2$N] used in this study was pre-equilibrated upon contact with aqueous solutions containing HNO$_3$ in different concentrations, which were the same with the HNO$_3$(aq) phase in the following extraction experiments. The HNO$_3$(aq) (2 mL) dissolving a nitrate salt of the desired M^{n+} (Pd(NO$_3$)$_2$·xH$_2$O, Rh(NO$_3$)$_3$·xH$_2$O 20 mM determined by Perkin Elmer Optima 3000 ICP-AES) was loaded in a test tube together with the pre-equilibrated [Hbet][Tf$_2$N] (2 mL), followed by vigorous shaking in a thermostat bath at 298 K for 1 h. It was preliminarily checked that the extraction of M^{n+} in the current systems is equilibrated within 10 min. Ruthenium(III) nitrosyl nitrate solution was only commercially available as a starting material of Ru(III), and using this solution the same operation has been done. After waiting for the phase separation, the concentrations of M^{n+} in the HNO$_3$(aq) phase were determined by ICP-AES. The extractability (*E*%) and distribution ratio (*D*) were calculated by the following equations, respectively.

$$E\% = 100 \times ([M^{n+}]_{ini} - [M^{n+}]_{aq})/[M^{n+}]_{ini} \qquad (1)$$

$$D = ([M^{n+}]_{ini} - [M^{n+}]_{aq})/[M^{n+}]_{aq} \qquad (2)$$

where [M^{n+}]$_{ini}$ and [M^{n+}]$_{aq}$ denote the M^{n+} concentrations in HNO$_3$(aq) at the initial state and after the extraction, respectively. The volumes of aqueous and IL phases are also taken into account in Eq. 2, although it does not appear in this equation because of the actual volume ratio equal to 1.

The left panel of Fig. 1 shows *E*% of Pd(II), Rh(III), and Ru(III) at the different [HNO$_3$]. As a result, the extraction of Pd(II) was almost quantitative, and most efficient in these three elements. Rhodium(III)
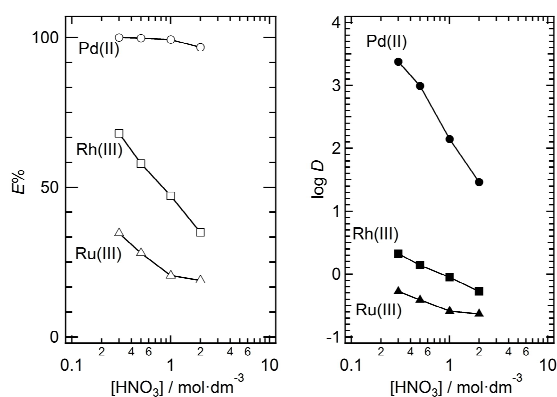
Fig. 1. Extractability ($E\%$, left) and distribution ratio (D, right) of Pd(II), Rh(III), and Ru(III) at different [HNO$_3$] in [Hbet][Tf$_2$N]-HNO$_3$(aq) system.

followed Pd(II), and $E\%$ of Ru(III) was the lowest. Furthermore, $E\%$ of Pd(II) shows very small variation at the different [HNO$_3$], while those of Rh(III) and Ru(III) clearly tend to decrease with an increase in [HNO$_3$]. The right panel of Fig. 1 obviously demonstrates that the extraction behaviours of all M^{n+} studied show the similar dependency on [HNO$_3$].

The results in Fig. 1 suggest that the low [HNO$_3$] is preferable to earn the high $E\%$ and D for each element. However, it seems to be necessary to pay attention to the other aspects of M^{n+} in the aqueous solution, hydrolysis. We performed the same extraction experiment at the lower [HNO$_3$] condition. At [HNO$_3$] = 0.01 M, black gel precipitate was found in the sample of Pd(II). Taking the stability of Pd(II) towards hydrolysis into account, this material could be Pd(OH)$_2$,[6] although any detailed characterization has not been carried out. According to the speciation simulations for Pd(II) and Rh(III), these M^{n+} hydrolyse at pH > 0.5 and > 1.4, respectively, and precipitate as Pd(OH)$_2$ and Rh$_2$O$_3$.[6] Although any critical hydrolysis constants of Ru(III) in HNO$_3$(aq) are not available on the database, Ru^{3+}(aq) hydrolyses at pH > 1. In summary, pH of the aqueous phase should be at least lower than 0.5, which is corresponding to [H$^+$] = 0.3 M (= [HNO$_3$]), to avoid the undesired hydrolysis of M^{n+}.

It is worthy to emphasize the efficiency of the Rh(III) extraction in the current system. Very limited studies have been performed in the former time, and low D values ranging from 10^{-3} to 10^{-1} were only reported so far.[7] Therefore, there is still room for improvement in the extraction of this precious and valuable element. In contrast, D of Rh(III) observed in the current system is ranging from 0.53 to 2.12. Thus, the higher extraction efficiency for Rh(III) than the former reports has been achieved in the present system. Recently, we studied the Rh(III) extraction in other IL-HNO$_3$(aq) systems containing some extractants, and reported the efficient extraction with D from 0.1 to 16.9.[8] The extractants we used previously do not always consist only of C, H, O, N, but sometimes also contain S and P. These heavy elements are not favourable in green chemistry, and may also be problematic in the succeeding processes to recover and reuse the separated metal resources. On the other hand, one does not have to add any extractants in the current system using [Hbet][Tf$_2$N], because [Hbet]$^+$ may also act as an extractant (*vide infra*). This point is much advantageous compared to other ordinary extraction methods relying extractants.

Using D obtained here, the separation factor (SF) for each pair of Pd(II), Rh(III), and Ru(III) at the given [HNO$_3$] was calculated. The results are shown in Fig. 2. In the combination of Pd(II) and Ru(III), the highest separation efficiency can be expected, *i.e.*, SF$_{Pd/Ru}$ = 4.5 × 10^3 at [HNO$_3$] = 0.3 M and 1.2 × 10^2 at [HNO$_3$] = 2.0 M. The separation of Pd(II) from Rh(III) is also effective as indicated by
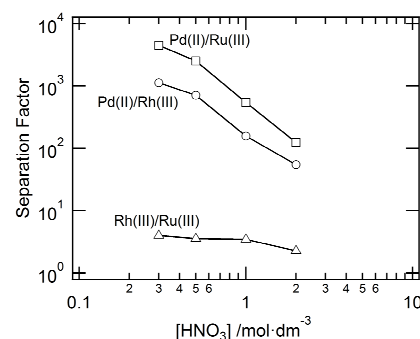

Fig. 2. Separation factors of Pd(II)/Ru(III), Pd(II)/Rh(III), and Rh(III)/Ru(III) at different [HNO$_3$] in [Hbet][Tf$_2$N]-HNO$_3$(aq) system.

SF$_{Pd/Rh}$ ranging from 1.1 × 10^3 to 5.4 × 10^1. The SF value of the Rh(III)/Ru(III) pair is just 2.3-4.0 in the studied [HNO$_3$] range, and does not show clear dependency on [HNO$_3$]. This is because of the similar slopes of these M^{n+} in the log D-log [HNO$_3$] plots (right panel of Fig. 1).

To obtain some mechanistic insights on the extraction behaviour of Pd(II), Rh(III), and Ru(III) in the current system, we also performed the similar extraction experiments in other IL-HNO$_3$(aq) systems. As ILs, Tf$_2$N$^-$ salts of choline (Me$_3$N$^+$CH$_2$CH$_2$OH) and trimethylpropylammonium (Me$_3$N$^+$CH$_2$CH$_2$CH$_3$, [TMPA]$^+$) cations were selected because of the similarity in the molecular structures with [Hbet]$^+$. Furthermore, these ILs are also enough hydrophobic to form an IL layer separated from water. Figure 3 shows log D of each M^{n+} as a function of [HNO$_3$] in the different IL-HNO$_3$(aq) systems.

Any significant extraction was not observed for Pd(II) in the tested [HNO$_3$] range of the [TMPA][Tf$_2$N]-HNO$_3$(aq) system at all, and hence no data points were plotted in Fig. 3. The [TMPA]$^+$ cation is not functionalized to interact with M^{n+}, and should be most hydrophobic in the tested three ILs. Therefore, neither coordination nor cation exchange reactions could be likely to occur in this system. The remaining possibility is an ion pair extraction. From the actual result, the non-charged complex like Pd(NO$_3$)$_2$, however, seems not to be formed significantly in the studied [HNO$_3$] region, or even if such a species is present in HNO$_3$(aq), it is not extractable to the IL phases. Therefore, the ion pair extraction is also ruled out from candidates of the extraction mechanism. This is also the case for the other IL-HNO$_3$(aq) systems, because the variation of log D as a function of [HNO$_3$] is different from that expected from the ion pair extraction, *i.e.*, the extraction should be enhanced with increasing [NO$_3^-$].
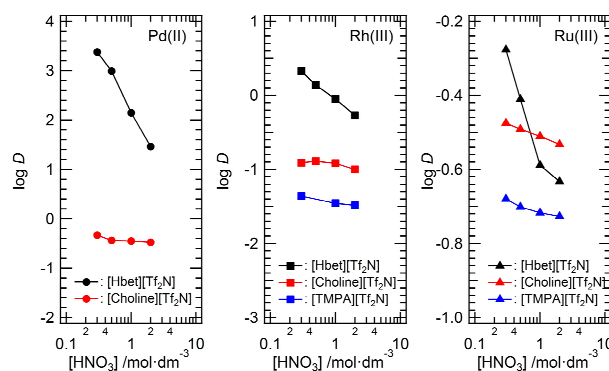

**Fig. 3.** Extraction behaviours of Pd(II) (left), Rh(III) (centre), and Ru(III) (right) at different [HNO$_3$] from the aqueous phase to [Hbet][Tf$_2$N] (black), [choline][Tf$_2$N] (red), and [TMPA][Tf$_2$N] (blue).

The higher extraction of Pd(II), which is however independent of [HNO_3], was observed in the [choline][Tf_2N]-HNO_3(aq) system. Considering that the deprotonation of the terminal hydroxyl group in [choline]$^+$ hardly occurs because of the very strong basicity of alkoxides, it should be reasonable to suppose that the extraction proceeds through an exchange reaction of Pd^{2+} with [choline]$^+$ between HNO_3(aq) and [choline][Tf_2N] phases, namely cation exchange mechanism (Eq. 3).

$$Pd^{2+}_{aq} + 2\,[choline]^+_{IL} = Pd^{2+}_{IL} + 2\,[choline]^+_{aq} \qquad (3)$$
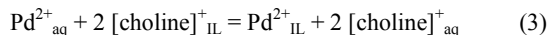
In contrast, the results in [Hbet][Tf_2N]-HNO_3(aq) is much different from the other two systems as described above, *i.e.*, log D decreases with increasing [HNO_3]. Taking the deprotonation of the carboxylic group in [Hbet]$^+$ and affinity of the resulting carboxylate for Pd^{2+} into account, a coordination species like [$Pd(bet)_m$]$^{2+}$ should be participated to the extraction. The strong coordination of the carboxylate to Pd^{2+} has been evidenced in a Pd^{2+}-CH_3COO^- system, that is, K_1 = [$Pd(CH_3COO)^+$]/[Pd^{2+}][CH_3COO^-] = $10^{4.34}$ at 298 K and 1 M ($NaClO_4$) ionic strength.[6a] It must be emphasized that the formed Pd^{2+}-bet complex has +2 charges regardless of the number of coordinating bet (*m*), because bet is a zwitterionic ligand, thus non-charged. Therefore, the cation exchange should also be present in the Pd(II) extraction process. The involved cationic species could be H^+ released from [Hbet]$^+$ in the formation of [$Pd(bet)_m$]$^{2+}$. The slope of the log D-log [HNO_3] plot for Pd(II) in Fig. 1 was evaluated as -2.4, implying two H^+ are left in the aqueous phase through the extraction. Thus, the coordination number of bet in the extracted species should also be 2. In summary, the extraction of Pd(II) in [Hbet][Tf_2N]-HNO_3(aq) undergoes the following reaction (Eq. 4).

$$Pd^{2+}_{aq} + 2[Hbet]^+_{IL} = [Pd(bet)_2]^{2+}_{IL} + 2\,H^+_{aq} \qquad (4)$$
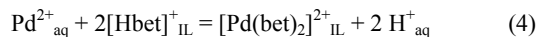
This proposed mechanism is in line with the observed tendency of log D towards [HNO_3]. An increase in [HNO_3] prevents the forward reaction of Eq. 4, and therefore the extraction of Pd(II) is supressed. The higher extraction efficiency of [Hbet][Tf_2N] than [choline][Tf_2N], which also extracts Pd(II) through the cation exchange reaction, indicates that the formation of [$Pd(bet)_m$]$^{2+}$ enhances the solubility of Pd^{2+} in the IL.

The similar tendencies were also observed in the extraction behaviours of Rh(III) in the different IL-HNO_3(aq) systems as shown in Fig. 3. In both systems other than [Hbet][Tf_2N], log D seems to be independent of [HNO_3]. Hence, the cation exchange reaction like Eq. 3 could be appropriate as an extraction mechanism. In contrast, the dependency on [HNO_3] in use of [Hbet][Tf_2N] implies that the Rh(III) extraction proceeds through the mechanism similar to Eq. 4, namely the coordination of bet to Rh^{3+}, followed by the cation exchange.

Regarding the least extractable Ru(III) in this study, log D more or less decreases with increasing [HNO_3]. The chemical speciation of Ru(III) in HNO_3(aq) is much more complicated than those of Pd(II) and Rh(III). The various nitrosyl nitrato Ru(III) complexes are known to occur in the HNO_3(aq).[9] Thus, association and dissociation of NO_3^- in Ru(III) species would also affect the extraction behaviour. This might be reason why log D in the [choline][Tf_2N]- and [TMPA][Tf_2N]-HNO_3 systems also exhibit the dependency on [HNO_3]. The additional coordination interaction of bet to Ru(III) can be expected from the steeper variation of log D in [Hbet][Tf_2N]-HNO_3(aq). We are collecting additional experimental evidences for further discussion to conclude the detailed extraction mechanism of Ru(III).

In this communication, we demonstrated the efficiency of [Hbet][Tf_2N] in the extraction of Pd(II), Rh(III), and Ru(III) from HNO_3(aq), and discussed the extraction mechanisms briefly by comparing the observed behaviour with that in the different ILs bearing the similar molecular structures. In conclusion, Pd(II) should be separated successfully from Rh(III) and Ru(III) because of the high separation factors (10^1-10^3). To conclude the mechanistic consideration, further quantitative experimental evidences are required. One of the most important data should be the stability constants of the M^{n+}-bet complexes, which are indicators of the coordination strengths between bet and M^{n+}. The molecular structures of the M^{n+}-bet complexes formed are also of interest to understand the behaviour in the extraction chemistry. Other aspects to approach the actual separation process more closely are rapid equilibration of the extraction by temperature-swinging above and below UCST and mutual separation of the studied platinoids from their mixture. Collection of such data is currently in progress.

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Pd(II), Rh(III), and Ru(III) can be separated mutually through extraction from HNO_3(aq) to [Hbet][Tf$_2$N] ionic liquid without any additional extractants.