Stoichiometry of Palladium Extraction in Ionic Liquid

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1. Introduction

Ionic liquids (ILs) are organic salts that are benign and are normally liquid at ambient temperature. ILs have been studied as green solvent to substitute conventional organic solvents in various research areas such as separation, synthesis and electrochemistry [1]. Recently, in this laboratory, ILs were studied to determine their efficiency for the extraction and electrochemical recovery of actinides and fission products. In this study, we used dibutyl sulfoxide (DBSO) as the extractant and 1-buty-3-methylimidazolium bis(trifluoromethanesulfonyl) imide (C_4mimTf_2N) as an IL extraction solvent, and we showed that IL obtained higher distribution ratios for palladium than conventional organic solvents, and observed a decline in distribution ratios of palladium acidity increased [2]. In our present study, the number of DBSO molecules involved in the metal complex was calculated. The stoichiometry was found to be 1:2.33 and 1:1.05 (M:L) in C_4mimTf_2N from 0.05 M and 5 M of nitric acid solution, respectively.

2. Experimental

2.1 Materials and method

DBSO and C_4mimTf_2N were obtained from Sigma-Aldrich. The extraction experiment was carried out by equilibrating the organic phase (0.003~1 M DBSO in C_4mimTf_2N) and the aqueous phase (1000 ppm of palladium in the desired HNO_3 concentration), with a phase ratio of 1:1 at 25℃. After equilibration, the solution was allowed to settle, and aqueous phase was separated from organic phase. The aqueous phase was used to determine the concentration of palladium by ICP-OES (Model No. PQ 9000 Elite). The distribution ratio of palladium (D_{Pd}) was calculated from the aqueous phase concentration and D_{Pd} value is defined in Eq. (1):
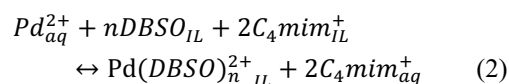
$$D_{Pd} = \frac{[Pd]_{IL}}{[Pd]_{aq}} = \frac{[Pd]_{aq,init} - [Pd]_{aq,fin}}{[Pd]_{aq,fin}} \qquad (1)$$

The species with the subscripts 'aq' and 'IL' refer to those in the aqueous and ionic liquid phase, and 'init' and 'fin' refer to those of before and after equilibration, respectively.

2.2 Results and discussion

The extraction of palladium with varying concentration of DBSO, from 0.003 to 1 M, from 0.05 M or 5 M nitric acid feed was investigated in C_4mimTf_2N and the results are presented in Fig. 1. An increment in palladium extraction with increasing DBSO concentration in C_4mimTf_2N was observed, which indicates that DBSO is participating in the extraction process.

Results show the extraction mechanism of palladium into C_4mimTf_2N can be best represented by a cation exchange reaction and its reaction is as follows:

$$Pd_{aq}^{2+} + nDBSO_{IL} + 2C_4mim_{IL}^{+}$$
$$\leftrightarrow Pd(DBSO)_n{}^{2+}{}_{IL} + 2C_4mim_{aq}^{+} \qquad (2)$$

The species with the subscripts 'aq' and 'IL' refer to those in the aqueous and ionic liquid phase
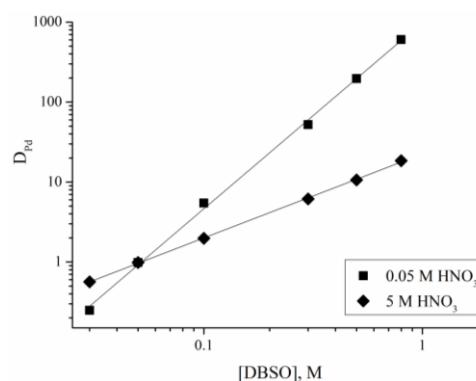

Fig. 1. Distribution ratio of palladium at varying DBSO concentrations extracted from 0.05 and 5 M HNO_3 feed into C_4mimTf_2N.
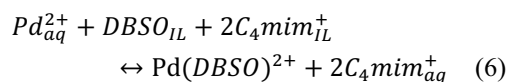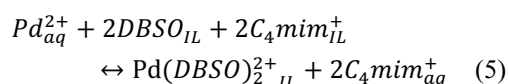
From eq. (2), the equilibrium constant for the extraction of palladium (K_{Pd}) can derived to Eq. (3):

$$K_{Pd} = \frac{[Pd(DBSO)_n^{2+}]_{IL}[C_4mim^+]_{aq}^2}{[Pd]_{aq}^{2+}[DBSO]_{IL}^n[C_4mim^+]_{IL}^2} \quad (3)$$

Substituting D_{Pd} for $[Pd(DBSO)_n^{2+}]_{IL}/[Pd]_{aq}$ and P_{Cnmim+} for $[C_4mim^+]_{aq}^2/[C_4mim^+]_{IL}^2$, and taking the logarithm and rearrange, one obtains

$$\log D_{Pd} = logK_{Pd} - logP_{C_nmim+} + nlog[DBSO] \quad (4)$$

A plot of $logD_{Pd}$ vs. the concentration of DBSO should result in straight lines with a slope 'n' and the intercept represents $logK_{Pd}$ - $logP_{Cnmim+}$ on the basis on Eq. (4). The slope 'n' represents the number of DBSO molecules associated with the metal complex during extraction. The slope 'n' for palladium extraction from 0.05 M and 5 M nitric acid feed was obtained from a slope analysis of the plot in Fig. 1. In case of DBSO in C_4mimTf_2N, the slope is 2.33 ± 0.04 from 0.05 M nitric acid feed and 1.05 ± 0.01 from 5 M nitric acid feed. In lower acidity (0.05 M HNO_3), extraction of mixed species of 1:2 as well as 1:3 M:L composition but 1:2 M:L composition is predominant, while in higher acidity (5 M HNO_3), 1:1 M:L composition is predominant. Extraction of mixed species has been reported previously in case of molecular diluents using TODGA [3]. Finally, the value of 'n' was obtained for the extraction of palladium from 0.05 M and 5 M nitric acid feeds Eq. (5) and Eq. (6), respectively.

$$Pd_{aq}^{2+} + 2DBSO_{IL} + 2C_4mim_{IL}^+$$
$$\leftrightarrow Pd(DBSO)_2^{2+}{}_{IL} + 2C_4mim_{aq}^+ \quad (5)$$

$$Pd_{aq}^{2+} + DBSO_{IL} + 2C_4mim_{IL}^+$$
$$\leftrightarrow Pd(DBSO)^{2+} + 2C_4mim_{aq}^+ \quad (6)$$

The number of DBSO molecules associated with the metal complex decreases as the feed acidity increases. This shows that the acid interferes with the metal-ligand complex formation. It is presumed that DBSO is protonated in the presence of the high nitric acid feed concentration, therefore, hydrogen ion competes with palladium ion, resulting in less DBSO molecules associated with the metal complex at higher acidity. The formation reaction of adducts of DBSO with nitric acid can be written such that

$$H_{aq}^+ + nDBSO_{IL} + C_4mim_{IL}^+$$
$$\leftrightarrow H(DBSO)_{n\,IL}^+ + C_4mim_{aq}^+ \quad (7)$$
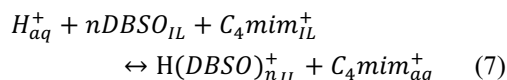
In the previous study [1], we extracted palladium from varying concentration of nitric acid (0.05~8 M HNO_3) into C_4mimTf_2N containing 0.1 M DBSO, and a sharp drop of D_{Pd} values was observed as the feed acidity increases. We can explain the extraction tendency of palladium obtained from the previous study as well by using the competing reaction between Palladium and hydrogen ions (shown in Eq. (7)) in this present paper.

3. Conclusions

Extraction of palladium using DBSO was carried out in varying DBSO concentration (0.003~8 M) in C_4mimTf_2N from 0.05 M and 5 M nitric acid feeds. The stoichiometry of palladium extraction in C_4mimTf_2N was obtained from a slope analysis of a plot ($logD_{Pd}$ vs. the concentration of DBSO). The results indicated that, in high acidity, palladium is coordinated with 1.05 DBSO molecules, compared to 2.33 molecules in low acidity, due to competition between palladium and hydrogen ions, and the results gave a clue to understand the extraction behavior of palladium in the previous study.

REFERENCES

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