

Extraction of Palladium(II) and Platinum(IV) from Hydrochloric Acid Solutions with Trioctylammonium Nitrate Ionic Liquid without Dilution

Shoichi Katsuta¹  · Junko Tamura¹

Received: 30 June 2017 / Accepted: 26 December 2017 / Published online: 6 April 2018
© Springer Science+Business Media, LLC, part of Springer Nature 2018

Abstract The fundamental properties and extraction capability of an ionic liquid (IL), trioctylammonium nitrate ([HTOA][NO₃]), for Pd^{II} and Pt^{IV}, are investigated. At room temperature, [HTOA][NO₃] is a solid (melting point: 30.7 °C), but it becomes a liquid (melting point: 16.7 °C) when saturated with water. Water-saturated [HTOA][NO₃] exhibits a viscosity of 267.1 mPa·s and an aqueous solubility of 2.821×10^{-4} mol·dm⁻³ at 25 °C, and can be used as an extraction solvent without dilution. [HTOA][NO₃] exhibits an extremely high extraction capability for Pd^{II} and Pt^{IV} in dilute hydrochloric acid (0.1–2 mol·dm⁻³ HCl); the distribution ratio reaches 3×10^4 for both the metals. From electrospray ionization mass spectrometry analysis, the species extracted in the IL phase are [PdCl₃]⁻ and [PdCl₂(NO₃)]⁻ for Pd^{II} and [PtCl₆]²⁻ and [PtCl₅]⁻ for Pt^{IV}. A majority of the other transition metals are considerably less or marginally extracted into [HTOA][NO₃] from a 0.1 mol·dm⁻³ hydrochloric acid solution. The extraction capacity of [HTOA][NO₃] is greater than that of other hydrophobic ILs such as [HTOA]Cl and bis(trifluoromethanesulfonyl)imide-based ILs. The metals extracted into the IL phase are quantitatively back-extracted using an aqueous solution containing thiourea and nitric acid. By controlling the thiourea concentration and shaking time, Pd^{II} and Pt^{IV} are mutually separated to some extent in the back extraction process. The IL phase used for the back extraction can be reused for the forward extraction of these metals after scrubbing it with an aqueous nitric acid solution.

Keyword Ionic liquid · Water-saturated trioctylammonium nitrate · Extraction · Palladium(II) · Platinum(IV)

✉ Shoichi Katsuta
katsuta@faculty.chiba-u.jp

¹ Department of Chemistry, Graduate School of Science, Chiba University, 1-33 Yayoi-cho, Inage, Chiba 263-8522, Japan

1 Introduction

Platinum-group elements are crucial metals used in industrial processes and products, jewelry, and dental materials [1]. Particularly, palladium, platinum, and rhodium are important as components in catalysts used for automobile exhausts and synthesis of organic chemicals. In addition, palladium and platinum also play a large role in fuel cell technology. Meanwhile, the worldwide demand for these metals is still increasing, which is not satisfied by their supply from natural resources; therefore, there is an increase in the requirement for recycling these metals from waste products [2].

Solvent extraction is one of the important methods to separate, refine, and recycle platinum-group elements in different industries [3]. Dialkyl sulfides and tributyl phosphate are agents typically used for extracting palladium and platinum from hydrochloric acid solutions [3, 4]. These agents are used by dissolving them in organic molecular solvents, leading to health, safety, and environmental problems. On the other hand, ionic liquids (ILs) have attracted attention as one of the alternatives to organic molecular solvents for solvent extraction, because ILs are recognized as green solvents [5].

In addition, ILs are also attractive because some of them exhibit a high extraction capability for ionic species [6–14]. The extraction capability of ILs is considerably dependent on the kind of constituent ions, the combinations of which are numerous. To obtain information regarding the rules governing the extraction capability of ILs for ions, the extraction behavior of several ions such as substituted phenolate [14–16], tetrachloroaurate [17], and paraquat ions [18] in various IL/aqueous biphasic systems has been investigated. The results revealed that the distribution ratio of each target ion is a function of the aqueous solubility of the IL used; the dependence can be explained on the basis of the extraction mechanism including ion exchange and ion-pair transfer processes with the IL constituent ions. Using an anionic species as the extraction target, for ILs with different anions and a certain cation, the extraction capability increases with an increase in the aqueous solubility of the IL; the opposite holds true for the ILs with different cations and a given anion. Long-chain alkylammonium salts of small inorganic anions such as methyltrioctylammonium chloride ([MTOA]Cl) and trioctylammonium chloride ([HTOA]Cl), which are known as organic anion exchangers, represent typical examples that are thought to exhibit a high extraction capability for an anion [19–21]. However, these compounds are solids or highly viscous liquids at room temperature. Hence, they are always used after being diluted with organic molecular solvents for the extraction purpose, although it is unfavorable to use any organic molecular solvent because of safety and environmental concerns. Organic anion exchangers diluted with organic molecular solvents such as toluene and kerosene are known to be effective for extracting platinum-group elements in hydrochloric acid solutions [22–25].

Neat ILs have been used as extracting phases for platinum group elements in aqueous chloride solutions, in which a majority of the metals exist as anionic chloride complexes [26–32]. Previously, our group has proposed the use of mixtures with two ILs, that is, trioctylammonium nitrate ([HTOA][NO₃]) and trioctylammonium bis(trifluoromethanesulfonyl)imide ([HTOA][NTf₂]) [28]. Here [HTOA][NO₃], which is expected to be an excellent anion exchanger, is a solid at room temperature; thus, [HTOA][NTf₂] is used as a diluent. For example, a mixture of 10 mass% [HTOA][NO₃] in [HTOA][NTf₂] exhibits a relatively low viscosity (235.7 mPa·s) when saturated with water at 25 °C and has a powerful, selective extraction capability for Pd^{II} and Pt^{IV} from dilute hydrochloric acid solutions. The use of IL mixtures is expected to exhibit the following merits: ILs exhibit higher hydrophobicity and lower viscosity compared to a pure liquid-ion exchanger; their

extraction capability, viscosity, and hydrophobicity can be controlled by the composition ratio; they are nonflammable and environmentally friendly because they only contain ions. In addition, the [HTOA] salts are so-called “protic ILs” that can be easily prepared by simple acid–base reactions of trioctylammonium (TOA) with HNO_3 and HNTf_2 .

If [HTOA][NO_3] were a hydrophobic, low-viscosity liquid, it could be used as a powerful extractant without any diluent. In this study, the extraction of Pd^{II} , Pt^{IV} , and some other heavy metals using water-saturated [HTOA][NO_3] from hydrochloric acid solutions was examined because [HTOA][NO_3] was found to become a liquid at room temperature when saturated with water, and its viscosity and aqueous solubility were sufficiently low (data are shown below). To the best of our knowledge, this is the first study in which [HTOA][NO_3] was used as a metal extractant without dilution. In addition, some other water-saturated ILs were examined for comparison. Fundamental properties such as melting point, density, viscosity, water content, and aqueous solubility of water-saturated [HTOA][NO_3] were also investigated.

2 Experimental Section

2.1 Reagents and Instruments

[HTOA][NO_3], [HTOA]Cl, [HTOA][NTf_2], and 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([BMIm][NTf_2]) were prepared according to a previously reported study [17, 28]. [MTOA]Cl with a > 97 mass% purity was purchased from Sigma–Aldrich and used as received. Methyltrioctylammonium nitrate ([MTOA][NO_3]) was prepared as follows: First, 50 cm³ of a benzene solution containing 1.0 mol·dm^{−3} of [MTOA]Cl was mixed with 50 cm³ of an aqueous solution containing 4.0 mol·dm^{−3} of sodium nitrate, and after centrifugation, the benzene phase was separated. This operation was carried out four times for the benzene solution to completely exchange Cl^- with NO_3^- . Furthermore, the benzene phase was washed five times with deionized water to remove Na^+ . Then, it was transferred to a boiling flask, evaporated to dryness using a rotary evaporator, and further dried over P_2O_5 under vacuum for 24 h to afford a pale-yellow solid (16.8 g, 78% yield). ¹H NMR (400 MHz, CDCl_3 , TMS): δ = 3.278–3.365 (t, 6H, CH_2), 3.148 (s, 3H, CH_3), 1.631–1.751 (m, 6H, CH_2), 1.258–1.425 (m, 30H, CH_2), 0.850–0.885 (t, 9H, CH_3). MS (ESI, acetonitrile, m/z): positive, 368.4240, [MTOA]⁺; negative, 492.4034, [MTOA][NO_3][−]. The amounts of Na^+ and Cl^- in the product were analyzed by atomic absorption spectrophotometry (AAS) and ion-selective potentiometry, respectively ($\text{Na}^+ < 3$ ppm, $\text{Cl}^- < 8$ ppm). Ultrapure or equivalent grade mineral acids (HCl and HNO_3) were purchased from Kanto Chemicals. Standard aqueous solutions of Mn^{II} , Fe^{III} , Co^{II} , Ni^{II} , Cu^{II} , Zn^{II} , Rh^{III} , Pd^{II} , and Pt^{IV} , purchased as 1000 ppm atomic absorption standards from Kanto Chemicals or Wako Pure Chemicals, were used after appropriate dilution. Dichloromethane and benzene (Kanto Chemicals, guaranteed reagent grade) were purified by distillation and triplicate washing with water, respectively. Sudan III (1-[(E)-{4-[(Z)-phenyldiazenyl]phenyl}diazenyl]-2-naphthol, Tokyo Chemical Industry, > 90 mass% purity), acetonitrile (Kanto Chemicals, LC/MS grade), and other reagents (Kanto Chemicals or Wako Pure Chemicals, guaranteed reagent grade) were used as received. Water was deionized and further purified using a Milli-Q Labo system (Millipore).

A Thermo Neslab RTE-7 thermocontrolled water bath and a Nihon Keiryō Kogyō No.1 primary standard thermometer (uncertainty = ± 0.03 K) were used for melting point

measurements. An Anton Paar DMA35n oscillating U-tube density meter, a Kusano No. 2B Ubbelohde-type glass viscometer (viscometer constant: $0.4718 \text{ nm}^2 \cdot \text{s}^{-2}$), and a Hir-anuma AQ-7 Karl–Fischer coulometric titrator were used for measurements of density, viscosity, and IL water content, respectively. UV–Vis spectrophotometry and AAS measurements were carried out on a Beckman DU-640 spectrophotometer and a Hitachi Z-6100 polarized Zeeman flame atomic absorption spectrophotometer, respectively. Potentiometric determination of Cl^- was carried out on a Horiba F-23 ion meter equipped with a #6560-10C Cl^- ion-selective electrode (ISE). The shaking and centrifugation of a centrifuge tube were carried out using a Taitec SR-1N reciprocal shaker ($190 \text{ strokes} \cdot \text{min}^{-1}$) and a Kubota 2010 tabletop centrifuge (3000 rpm) with an RS-240 swing rotor, respectively. ^1H NMR and mass spectral measurements were carried out on a JEOL JNM-ECS400 FT-NMR spectrometer and a Thermo-Fisher Exactive mass spectrometer, respectively, at the Center for Analytical Instrumentation, Chiba University.

2.2 Measurements of Fundamental Properties of Water-Saturated ILs

The melting point of water-saturated [HTOA][NO_3] and the density, viscosity, water content, and aqueous solubility of water-saturated [HTOA][NO_3], [HTOA]Cl, [MTOA][NO_3], and [MTOA]Cl were determined. First, the IL was equilibrated with water in a thermostatic water bath at $25 \pm 0.05 \text{ }^\circ\text{C}$, and its melting point was measured by the rising melting point method. The density was measured at $25 \pm 0.2 \text{ }^\circ\text{C}$ using a density meter, which was calibrated using pure water. Kinematic viscosity was measured at $25 \pm 0.05 \text{ }^\circ\text{C}$ using a Ubbelohde viscometer calibrated by the manufacturer, and the dynamic viscosity was calculated as the product of the kinematic viscosity and density. The water content was measured by a Karl–Fischer titration, and the concentration of the IL cation in the aqueous phase was measured by the ion-pair extraction and spectrophotometric method using bis[2-(5-bromo-2-pyridylazo)-5-(*N*-propyl-*N*-sulfo-propyl-amino)phenolato]cobaltate(III) [33].

The volume change of the IL phase from the equilibration of water-saturated [HTOA][NO_3] with hydrochloric acid solutions was evaluated as follows. A solution of $5.0 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$ Sudan III dissolved in water-saturated [HTOA][NO_3] was prepared. The IL solution of Sudan III was equilibrated with a 100-fold volume of a hydrochloric acid solution ($0.10\text{--}2.0 \text{ mol} \cdot \text{dm}^{-3}$ HCl) in a centrifuge tube by mechanically shaking the tube in a thermostatic chamber at $25 \pm 0.2 \text{ }^\circ\text{C}$. Following centrifugation for complete phase separation, the tube was allowed to stand for more than 15 min in a thermostatic water bath at $25 \pm 0.05 \text{ }^\circ\text{C}$. The IL phases before and after shaking were diluted to greater than 20-fold with ethanol, and the Sudan III concentrations were spectrophotometrically determined ($\lambda_{\text{max}} = 507.0 \text{ nm}$, $\epsilon = (3.15 \pm 0.07) \times 10^{-4} \text{ cm}^{-1} \cdot \text{mol}^{-1} \cdot \text{dm}^3$ in ethanol at $25 \text{ }^\circ\text{C}$). It was separately confirmed that the partition of Sudan III into the aqueous phase was negligibly small.

In addition, the density of the IL phase, the concentration of Cl^- in the IL phase, and the concentrations of [HTOA] $^+$ and [NO_3] $^-$ in the aqueous phase were determined for the [HTOA][NO_3]–hydrochloric acid biphasic system. The density and [HTOA] $^+$ concentration were measured in the same manner as described above. The concentration of NO_3^- in the aqueous phase was determined by the spectrophotometric method using brucine (2,3-dimethoxystrychnidin-10-one) [34]. The concentration of Cl^- in the IL phase was determined as follows. A portion of the IL phase was placed in a separate tube and mechanically shaken for 1 h with a 10-fold volume of a $1.0 \text{ mol} \cdot \text{dm}^{-3}$ aqueous HNO_3 solution; by this

operation, Cl^- in the IL phase was quantitatively back-extracted into the aqueous HNO_3 solution. After centrifugation, a portion of the HNO_3 phase was pipetted out and neutralized using an aqueous NaOH solution. The Cl^- concentration was measured by an ISE.

2.3 Forward Extraction of Metal Ions

Aqueous solutions containing $0.10\text{--}2.0\text{ mol}\cdot\text{dm}^{-3}$ HCl and metal ions were prepared and stored for greater than 24 h at room temperature; the metal concentrations were 1.0×10^{-4} to $7.3 \times 10^{-4}\text{ mol}\cdot\text{dm}^{-3}$ for Pd; $9.7 \times 10^{-5}\text{ mol}\cdot\text{dm}^{-3}$ for Rh; 7.4×10^{-5} to $5.4 \times 10^{-4}\text{ mol}\cdot\text{dm}^{-3}$ for Pt; $1.0 \times 10^{-4}\text{ mol}\cdot\text{dm}^{-3}$ for Co and Ni; $9.6 \times 10^{-5}\text{ mol}\cdot\text{dm}^{-3}$ for Zn; $9.8 \times 10^{-5}\text{ mol}\cdot\text{dm}^{-3}$ for Cu; $1.1 \times 10^{-4}\text{ mol}\cdot\text{dm}^{-3}$ for Mn and Fe. A certain amount of a water-saturated IL was weighed in a centrifuge tube; the volume was calculated from the mass using the density (Table 1). A 100-fold volume of the hydrochloric acid solution of a metal ion was added to the centrifuge tube. The tube was mechanically shaken for 15 min to 2 h in a thermostatic chamber at $25 \pm 0.2\text{ }^\circ\text{C}$. After centrifugation, the tube was allowed to stand for more than 15 min in a thermostatic water bath at $25 \pm 0.05\text{ }^\circ\text{C}$. The metal ion in the aqueous phase was determined by AAS in the flame mode (for Zn) or the graphite furnace mode (for other metals). The extraction percentage ($\%E$) and the distribution ratio (D) were calculated from the following equations:

$$\%E = 100 \left(\frac{C_{\text{aq}}^{\text{o}} - C_{\text{aq}}}{C_{\text{aq}}^{\text{o}}} \right) \quad (1)$$

$$D = \left(\frac{V_{\text{aq}}}{V_{\text{IL}}} \right) \left(\frac{C_{\text{aq}}^{\text{o}} - C_{\text{aq}}}{C_{\text{aq}}} \right) \quad (2)$$

Here, C_{aq}^{o} and C_{aq} represent the concentrations of metals in the aqueous phase before and after extraction, respectively, and V_{aq} and V_{IL} are the volumes of the aqueous and IL phases, respectively.

Table 1 Fundamental properties of water-saturated ILs at $25\text{ }^\circ\text{C}$

IL	Density ($\text{g}\cdot\text{cm}^{-3}$)	Viscosity ($\text{mPa}\cdot\text{s}$)	Solubility of water (mass%)	Solubility in water ^a ($\text{mol}\cdot\text{dm}^{-3}$)
[HTOA][NO_3]	0.9186 ± 0.0001	267.1 ± 0.1	2.81 ± 0.03	0.0002821 ± 0.0000004
[HTOA]Cl	0.8903 ± 0.0000	183.0 ± 0.1	7.6 ± 0.2	0.000394 ± 0.000003
[HTOA][NTf_2]	1.1018 [28]	179.4 [28]	1.02 [28]	0.0000063 [28]
[MTOA][NO_3]	0.9317 ± 0.0000	153.3 ± 0.0	7.6 ± 0.1	0.00116 ± 0.00001
[MTOA]Cl	0.9206 ± 0.0001	85.4 ± 0.1	25.1 ± 0.1	0.00557 ± 0.00005
[MTOA][NTf_2]	1.1100 [28]	485.4 [28]	0.287 [28]	0.0000256 [28]
[BMIm][NTf_2]	1.3919 [35]		1.4 [35]	0.01643 [28]

Each uncertainty represents the standard error of the mean from 3 to 6 independent experiments

^aConcentrations of IL component cations

2.4 Mass Spectrometric Analysis of the IL Phase after Extraction

A centrifuge tube, in which a $0.10 \text{ mol}\cdot\text{dm}^{-3}$ hydrochloric acid solution containing $1.0 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$ of Pd^{II} or $1.1 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$ of Pt^{IV} and water-saturated [MTOA][NO₃] were placed in a volume ratio of 100 : 1, was mechanically shaken for 1 h at 25 °C. After centrifugation, a portion of the IL phase was transferred to a sample vial, diluted to ~ 2000-fold with acetonitrile, and subjected to electrospray ionization mass spectrometry (ESI–MS) analysis.

2.5 Back Extraction of Metal Ions

An aliquot of the IL phase after the forward extraction was transferred to another centrifuge tube, to which a 10-fold volume of a stripping solution was added. Here, the stripping solutions examined were as follows: $1.0 \text{ mol}\cdot\text{dm}^{-3}$ HCl; $1.0 \text{ mol}\cdot\text{dm}^{-3}$ HNO₃; $1.0 \text{ mol}\cdot\text{dm}^{-3}$ thiourea; $1.0 \text{ mol}\cdot\text{dm}^{-3}$ thiourea and $1.0 \text{ mol}\cdot\text{dm}^{-3}$ HCl; $0.10\text{--}1.0 \text{ mol}\cdot\text{dm}^{-3}$ thiourea and $1.0 \text{ mol}\cdot\text{dm}^{-3}$ HNO₃. The tube was mechanically shaken for 5 min to 4 h at 25 ± 0.2 °C. After centrifugation, the aqueous phase was subjected to AAS. The back extraction percentage ($\%E_{\text{back}}$) was calculated as follows:

$$\%E_{\text{back}} = 100 \left(\frac{V_{\text{B,aq}} C_{\text{B,aq}}}{V_{\text{B,IL}} C_{\text{B,IL}}^0} \right) \quad (3)$$

where $C_{\text{B,IL}}^0$ and $C_{\text{B,aq}}$ represent the concentrations of metals in the IL phase before back extraction and in the aqueous phase after back extraction, respectively, and $V_{\text{B,aq}}$ and $V_{\text{B,IL}}$ are the volumes of the aqueous and IL phases used for back extraction, respectively.

3 Results and Discussion

3.1 Fundamental Properties of Water-Saturated ILs

Water saturated [HTOA][NO₃] is a liquid at room temperature and its melting point was determined to be 16.7 ± 0.8 °C; this value is lower than that of dry [HTOA][NO₃], 30.7 °C [28]. Table 1 summarizes the values of density, viscosity, water content, and aqueous solubility. In addition, the data for other water-saturated ILs, including literature values [28, 35], are summarized. All of these ILs are liquids at 25 °C when saturated with water.

The densities of the Cl[−]- and NO₃[−]-based ILs are less than $1 \text{ g}\cdot\text{cm}^{-3}$, that is, around the density of water, whereas those of the [NTf₂][−]-based ILs are greater than $1 \text{ g}\cdot\text{cm}^{-3}$. The viscosity of water-saturated [MTOA][NO₃] is comparable to that of [BMIm][PF₆] (249.6 mPa·s when dried [36]), showing that water-saturated [MTOA][NO₃] can be used as a solvent for extraction without any viscosity issues. All of the other water-saturated ILs, except for [MTOA][NTf₂] (485.4 mPa·s [28]), are even less viscous.

For a given cation, the content of water in the IL increases with the anion hydrophilicity as expected from the Gibbs energy for the transfer of the anion from water to nitrobenzene [37]: [NTf₂][−] < NO₃[−] < Cl[−]. In addition, the aqueous solubility of the IL increases in the same order. For the [NTf₂][−]-based ILs, the water content increases in the order of [MTOA]⁺ < [HTOA]⁺ < [BMIm]⁺, whereas the aqueous solubility increases in the order of [HTOA]⁺ < [MTOA]⁺ < [BMIm]⁺. These orders mostly correspond to the

hydrophilicity order of the cations as expected from the chemical structures, that is, $[\text{MTOA}]^+ < [\text{HTOA}]^+ < [\text{BMIIm}]^+$. However, the water content and aqueous solubility of Cl^- - or NO_3^- -based ILs are greater for $[\text{MTOA}]^+$ than for $[\text{HTOA}]^+$, which is difficult to explain by the hydrophilicity order of the cations. The unexpectedly low water content and aqueous solubility of $[\text{HTOA}]^+$ -based ILs are possibly related to the strong hydrogen bond interactions of the protic cation with the anions. The aqueous solubility of $[\text{HTOA}][\text{NO}_3]$ is comparable to that of hexane ($6.5 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$ [38]) and less than that of 1-octanol ($4.13 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$ [38]) and that of chloroform ($6.8 \times 10^{-2} \text{ mol}\cdot\text{dm}^{-3}$ [38]). Therefore, water-saturated $[\text{HTOA}][\text{NO}_3]$ is sufficiently hydrophobic to be used as an extraction solvent.

For the $[\text{HTOA}][\text{NO}_3]$ -hydrochloric acid biphasic system (IL/aqueous volume ratio = 1/100), the volume change and density of the IL phase, the concentrations of $[\text{HTOA}]^+$ and NO_3^- in the aqueous phase, and the concentration of Cl^- in the IL phase were evaluated. This biphasic system is the same as that used for the extraction of metals. Table 2 summarizes the results. With the increase in the initial HCl concentration, the aqueous equilibrium concentration of $[\text{HTOA}]^+$ decreases, whereas that of NO_3^- increases; therefore, the molar amount transferred from the IL phase to the aqueous phase is always greater for NO_3^- than for $[\text{HTOA}]^+$. On the other hand, at equilibrium, the concentration of Cl^- in the IL phase increases with the initial concentration of HCl in the aqueous phase. The above results indicate a partial anion exchange between the IL and aqueous phases. The amount of NO_3^- exchanged with Cl^- is estimated to be $\sim 30 \text{ mol}\%$ of the total amount of NO_3^- at an aqueous HCl concentration of $2.0 \text{ mol}\cdot\text{dm}^{-3}$. The volume change of the IL phase from water-saturated $[\text{HTOA}][\text{NO}_3]$ to that equilibrated with a 100-fold volume of the hydrochloric acid solution is negligibly small (from -1.8 to 1.4%), related to the extremely small loss of $[\text{HTOA}]^+$ into the aqueous phase and the small volume fraction of the anions in the IL phase.

3.2 Forward Extraction of Metal Ions

Forward extraction with water-saturated $[\text{HTOA}][\text{NO}_3]$ was carried out for $1 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$ Pd^{II} and Pt^{IV} in hydrochloric acid solutions (0.10 , 1.0 , or $2.0 \text{ mol}\cdot\text{dm}^{-3}$ HCl) with an IL/aqueous volume ratio of 1/100. It was preliminarily confirmed that the values of D for these metals are not influenced by the standing time of the aqueous phase before extraction (0 – 240 h) and the time of shaking for extraction (15 – 120 min). Table 3 summarizes the D and $\%E$ values at different HCl concentrations. Except for Pt^{IV} at $0.10 \text{ mol}\cdot\text{dm}^{-3}$ HCl, these metals are quantitatively extracted ($\%E \geq 99\%$) over all concentrations of HCl; the $\%E$ value of Pt^{IV} at $0.10 \text{ mol}\cdot\text{dm}^{-3}$ HCl is slightly lower (91%). The maximum D values observed are 3.2×10^4 for Pd^{II} (at $1.0 \text{ mol}\cdot\text{dm}^{-3}$ HCl) and 2.8×10^4 for Pt^{IV} (at $2.0 \text{ mol}\cdot\text{dm}^{-3}$ HCl). From the maximum D values, the $\%E$ values of Pd^{II} and Pt^{IV} are both estimated to be 97% for a volume ratio of 1/1000 for the IL phase to the aqueous phase, indicating that greater than 1000 fold enrichment of these metals is possible using $[\text{HTOA}][\text{NO}_3]$. Indeed, the $\%E$ value of Pd^{II} determined experimentally with an IL/aqueous volume ratio of 1/1000 was 97% from $1.0 \text{ mol}\cdot\text{dm}^{-3}$ HCl.

In addition, Table 3 summarizes the D and $\%E$ values of other metals. Zn^{II} and Fe^{III} are well extracted at 1.0 and $2.0 \text{ mol}\cdot\text{dm}^{-3}$ HCl, but the $\%E$ values at $0.1 \text{ mol}\cdot\text{dm}^{-3}$ HCl are 50 and 11% , respectively. The $\%E$ values of Mn^{II} , Co^{II} , Ni^{II} , Cu^{II} , and Rh^{III} are less than or equal to $\sim 10\%$ at $0.1 \text{ mol}\cdot\text{dm}^{-3}$ HCl. Therefore, an HCl concentration of $0.1 \text{ mol}\cdot\text{dm}^{-3}$ is suitable for the selective extraction of Pd^{II} and Pt^{IV} .

Table 2 Volume change and density of the IL phase, concentrations of [HTOA]⁺ and NO₃⁻ in the aqueous phase, and Cl⁻ concentration in the IL phase after equilibration of water-saturated [HTOA][NO₃] with hydrochloric acid at 25 °C

Initial concentration of HCl in aq. phase (mol·dm ⁻³)	Volume change of IL phase (%)	Density of IL phase ^a (g·cm ⁻³)	Equilibrium concentration of [HTOA] ⁺ in aq. phase ^a (mol·dm ⁻³)	Equilibrium concentration of NO ₃ ⁻ in aq. phase ^a (mol·dm ⁻³)	Equilibrium concentration of Cl ⁻ in IL phase ^a (mol·dm ⁻³)
0.10	- 1.3	0.9097 ± 0.0001	0.000075 ± 0.000001	0.00483 ± 0.0014	0.199 ± 0.000
1.0	1.4	0.9017 ± 0.0000	0.000044 ± 0.000002	0.00512 ± 0.0008	0.543 ± 0.001
2.0	- 1.8	0.9009 ± 0.0000	0.000031 ± 0.000009	0.00651 ± 0.0003	0.797 ± 0.002

IL/aqueous volume ratio = 1/100

^aEach uncertainty represents the standard error of the mean from 3 independent experiments

Table 3 Distribution ratios and extraction percentages of metals with water-saturated [HTOA][NO₃] from hydrochloric acid of different concentrations at 25 °C

Initial concentration of HCl in aq. phase (mol·dm ⁻³)	Mn ^{II}		Fe ^{III}		Co ^{II}		Ni ^{II}		Cu ^{II}	
	<i>D</i>	% <i>E</i>	<i>D</i>	% <i>E</i>	<i>D</i>	% <i>E</i>	<i>D</i>	% <i>E</i>	<i>D</i>	% <i>E</i>
0.10	0.0	0.0	13	11	1.9	1.8	1.1	1.1	10	9.4
1.0	5.0	4.8	5.1 × 10 ²	84	3.9	3.8	0.0	0.0	0.0	0.0
2.0	7.4	6.9	5.5 × 10 ³	98	3.8	3.6	6.9	6.5	20	17

Initial concentration of HCl in aq. phase (mol·dm ⁻³)	Zn ^{II}		Rh ^{III}		Pd ^{II}		Pt ^{IV}	
	<i>D</i>	% <i>E</i>	<i>D</i>	% <i>E</i>	<i>D</i>	% <i>E</i>	<i>D</i>	% <i>E</i>
0.10	98	50	15	13	2.4 × 10 ⁴	100	9.6 × 10 ²	91
1.0	3.2 × 10 ³	97	18	15	3.2 × 10 ⁴	100	2.3 × 10 ⁴	100
2.0	1.9 × 10 ⁴	99	20	17	1.4 × 10 ⁴	99	2.8 × 10 ⁴	100

Initial metal concentration in the aqueous phase = 9.6 × 10⁻⁵ to 1.1 × 10⁻⁴ mol·dm⁻³; IL/aqueous volume ratio = 1/100; shaking time = 1 h

The extractability order of the metal ions (except for kinetically inert Rh^{III}) corresponds to that of the stability of chloro complexes in the aqueous solution [39]. For example, in a 0.1 mol·dm⁻³ hydrochloric acid solution, 99% of Pd^{II} exists as [PdCl₃]⁻ and [PdCl₄]²⁻, whereas almost 100% of Ni^{II} exists as the aqua complex, [Ni(H₂O)₆]²⁺. To evaluate the extracted species of Pd^{II} and Pt^{IV}, ESI–MS spectra of the IL phase after extraction were recorded. The spectra obtained in the positive-ion mode exhibited only peaks corresponding to the IL constituent ions. Figures 1 (Pd) and 2 (Pt) show the spectra obtained in the negative-ion mode. In the spectra, there are the peak groups corresponding to [PdCl₃]⁻ (calculated monoisotopic *m/z* = 210.8100) and [PdCl₂(NO₃)]⁻ (237.8290) for Pd^{II} (Fig. 1) and those corresponding to [PtCl₆]²⁻ (202.3890), [PtCl₅]⁻ (369.8090), and [HTOA][PtCl₆]⁻ (759.1879) for Pt^{IV} (Fig. 2). In these species, [PdCl₃]⁻, [PdCl₂(NO₃)]⁻, and [PtCl₅]⁻ are coordinatively unsaturated; therefore, they possibly exhibit weak coordination of a water molecule in the IL phase. Previously [40], the extracted species of Pd^{II} and Pt^{IV} with chloroform solutions of quaternary ammonium chlorides were thought to be [PdCl₃]⁻, [PdCl₄]²⁻, and [PtCl₆]²⁻ from the analysis of the extraction data. The result based on ESI–MS indicate that the extracted species in the present extraction system are more complicated.

The extractability of Pd^{II} and Pt^{IV} from 0.1 mol·dm⁻³ hydrochloric acid solutions to water-saturated [HTOA][NO₃] was investigated with different metal ion concentrations. Figure 3 shows the *D* values as a function of the initial metal concentration in the aqueous phase. There is no significant dependence of *D* on the metal concentration. This result is consistent with the fact that the extracted species are all mononuclear complexes.

To compare the extraction capabilities of different ILs, the extractability of Pd^{II} and Pt^{IV} from 0.1 mol·dm⁻³ hydrochloric acid solutions to several water-saturated ILs was investigated. Table 4 summarizes the *D* and %*E* values, where the data for [MTOA]Cl are absent because the aqueous phase changed to cloudy due to the formation of micro-emulsions. The extractability is clearly considerably dependent on the IL: extractability increases in the order of [BMIm][NTf₂] < [MTOA][NTf₂] < [HTOA][NTf₂] < [HTOA]Cl < [MTOA][NO₃] < [HTOA][NO₃] for Pd^{II} and [BMIm][NTf₂] < [MTOA][NTf₂] < [HTOA][NTf₂] < [HTOA]Cl < [HTOA][NO₃] < [MTOA][NO₃] for Pt^{IV}. The

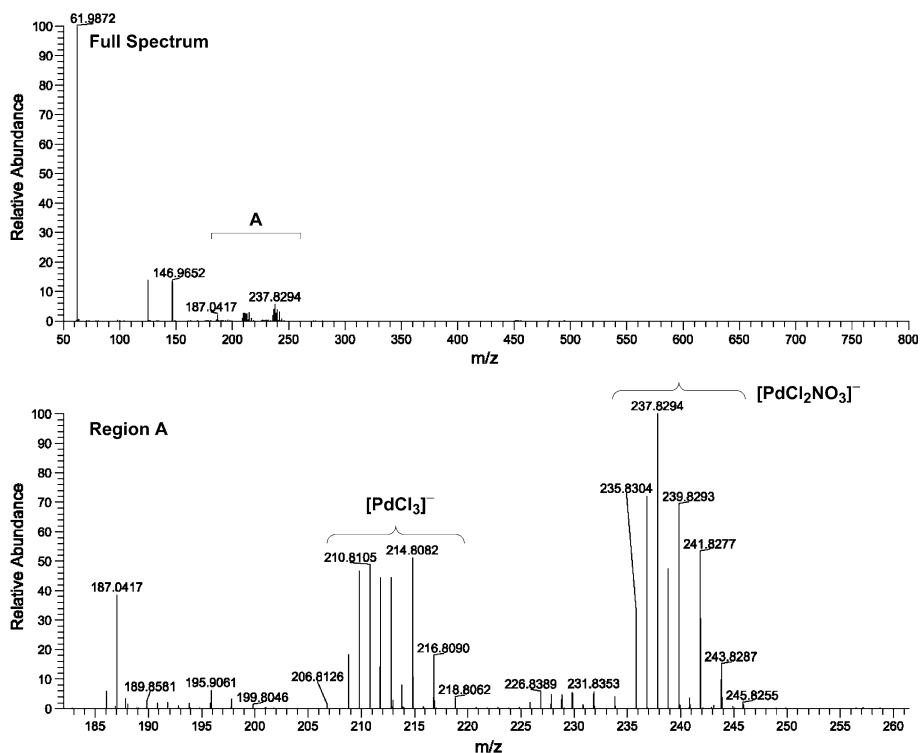


Fig. 1 Negative-ion ESI-MS spectra of the IL phase (diluted with acetonitrile) after the extraction of 1.0×10^{-5} mol·dm $^{-3}$ Pd II in 0.10 mol·dm $^{-3}$ hydrochloric acid with a 1/100 volume of [HTOA][NO $_3$]. Measuring range: $m/z = 50$ –800

extraction capability of [HTOA][NO $_3$] is the highest for Pd II and the second highest for Pt IV . As described in the Introduction, for the ILs composed of different anions and a specific cation, the extraction capability for a target anion increases with the increase in the IL aqueous solubility; the opposite holds true for the ILs composed of different cations and a specific anion [14–17]. The above orders of the ILs are almost consistent with those expected from the aqueous solubility values of the ILs (Table 1). This fact also supported that Pd II and Pt IV are extracted as anionic species. The higher extraction capability of [HTOA][NO $_3$] compared with that of [HTOA]Cl is not expected. Particularly, for the extraction of Pd II , the D value with [HTOA][NO $_3$] is more than 20-fold greater than that with [HTOA]Cl, possibly related to the extraction of [PdCl $_2$ (NO $_3$)] $^-$ as suggested by the ESI-MS analysis. In addition, notably, Pt IV is extracted to a greater extent compared to Pd II using [BMIm][NTf $_2$] and [MTOA][NTf $_2$], whereas Pd II is extracted with the other ILs to a greater extent although the reason is not clear at this stage.

3.3 Back Extraction of Pd and Pt

Some aqueous stripping solutions were examined for the back extraction of Pd II and Pt IV from the [HTOA][NO $_3$] phase after forward extraction. The IL/aqueous volume ratio and shaking time for back extraction were kept constant at 1/10 and 1 h, respectively. Table 5 summarizes the % E_{back} values. Pd II and Pt IV are not back-extracted or marginally back-

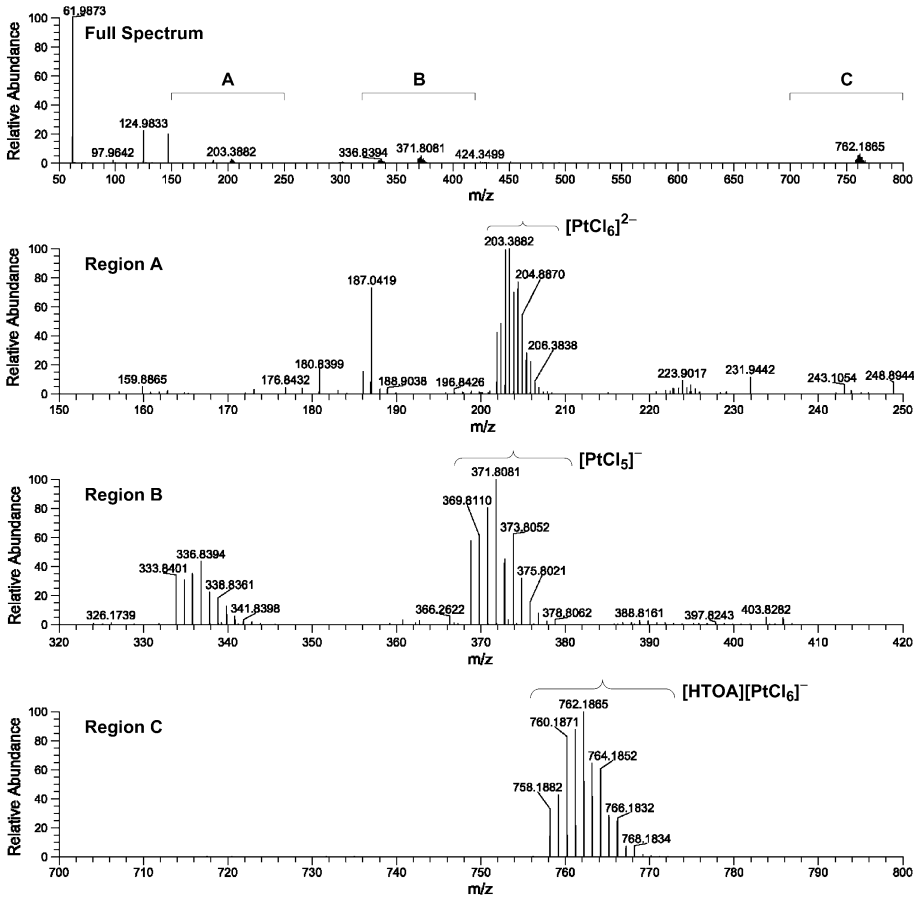


Fig. 2 Negative-ion ESI-MS spectra of the IL phase (diluted with acetonitrile) after the extraction of $1.1 \times 10^{-5} \text{ mol}\cdot\text{dm}^{-3} \text{ Pt}^{\text{IV}}$ in $0.10 \text{ mol}\cdot\text{dm}^{-3}$ hydrochloric acid with a 1/100 volume of $[\text{HTOA}][\text{NO}_3]$. Measuring range: $m/z = 50\text{--}800$

Fig. 3 Distribution ratios of Pd^{II} (filled circle) and Pt^{IV} (open triangle) as a function of the initial metal concentration in the aqueous phase ($0.10 \text{ mol}\cdot\text{dm}^{-3}$ hydrochloric acid). IL/aqueous volume ratio: 1/100. Shaking time: 1 h

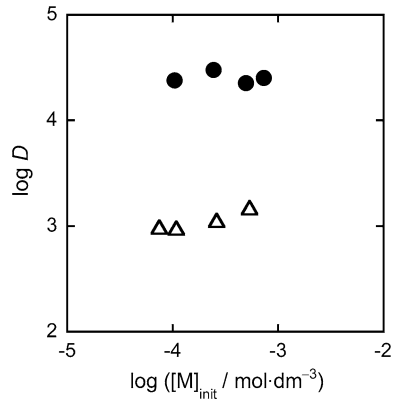


Table 4 Distribution ratios and extraction percentages of Pd^{II} and Pt^{IV} with different ILs from 0.10 mol·dm⁻³ hydrochloric acid at 25 °C

IL	Pd ^{II}		Pt ^{IV}	
	<i>D</i>	% <i>E</i>	<i>D</i>	% <i>E</i>
[HTOA][NO ₃]	2.4 × 10 ⁴	100	9.6 × 10 ²	91
[MTOA][NO ₃]	1.7 × 10 ⁴	99	5.9 × 10 ³	98
[HTOA]Cl	1.1 × 10 ³	91	4.6 × 10 ²	82
[HTOA][NTf ₂] [26]	16	14	6.3	5.9
[MTOA][NTf ₂] [26]	2.5	2.5	3.3	3.2
[BMIm][NTf ₂] [26]	0.05	0.05	2.1	2.1

Initial metal concentration in the aqueous phase = 1.0 × 10⁻⁴ mol·dm⁻³ (Pd^{II}), 1.1 × 10⁻⁴ mol·dm⁻³ (Pt^{IV}); IL/aqueous volume ratio = 1/100; shaking time = 1 h

Table 5 Back-extraction percentages of Pd^{II} and Pt^{IV} from IL phase with different aqueous stripping solutions at 25 °C

Aqueous stripping solution	% <i>E</i> _{back}	
	Pd ^{II}	Pt ^{IV}
1.0 mol·dm ⁻³ HCl	0.0	0.1
1.0 mol·dm ⁻³ HNO ₃	1.8	3.1
1.0 mol·dm ⁻³ thiourea	100	79
1.0 mol·dm ⁻³ thiourea + 1.0 mol·dm ⁻³ HCl	97	77
1.0 mol·dm ⁻³ thiourea + 1.0 mol·dm ⁻³ HNO ₃	100	87

Initial metal concentration in the IL phase = 1.0 × 10⁻² mol·dm⁻³ (Pd^{II}), 9.4 × 10⁻³ mol·dm⁻³ (Pt^{IV}); IL/aqueous volume ratio = 1/10; shaking time = 1 h

extracted with a 1.0 mol·dm⁻³ HCl or HNO₃ aqueous solution, respectively. On the other hand, a 1.0 mol·dm⁻³ aqueous thiourea solution exhibits an extremely good back extraction efficiency for these metals. An aqueous solution containing both 1.0 mol·dm⁻³ of thiourea and 1.0 mol·dm⁻³ of HNO₃ exhibits a higher back extraction efficiency, probably related to anion exchange, that is, the exchange of the chloro-complex anions of the metals in the IL phase with NO₃⁻ in the aqueous phase. However, an aqueous solution containing both 1.0 mol·dm⁻³ of thiourea and 1.0 mol·dm⁻³ of HCl exhibits a lower back extraction efficiency compared with that of an aqueous solution containing only 1.0 mol·dm⁻³ of thiourea, because Cl⁻ contributes to the forward extraction of these metals. In addition, back extraction experiments of Pd^{II} and Pt^{IV} were conducted using 1.0 mol·dm⁻³ aqueous HNO₃ solutions containing different concentrations of thiourea (0.10 and 0.50 mol·dm⁻³). Basically, the %*E*_{back} values of the metals decrease with a decrease in the thiourea concentration, but Pd^{II} is quantitatively back-extracted even at a thiourea concentration of 0.50 mol·dm⁻³. The %*E*_{back} value is always greater for Pd^{II} than for Pt^{IV}.

The effect of the shaking time for back extraction with an aqueous solution containing 0.50 mol·dm⁻³ of thiourea and 1.0 mol·dm⁻³ of HNO₃ was evaluated at an IL/aqueous

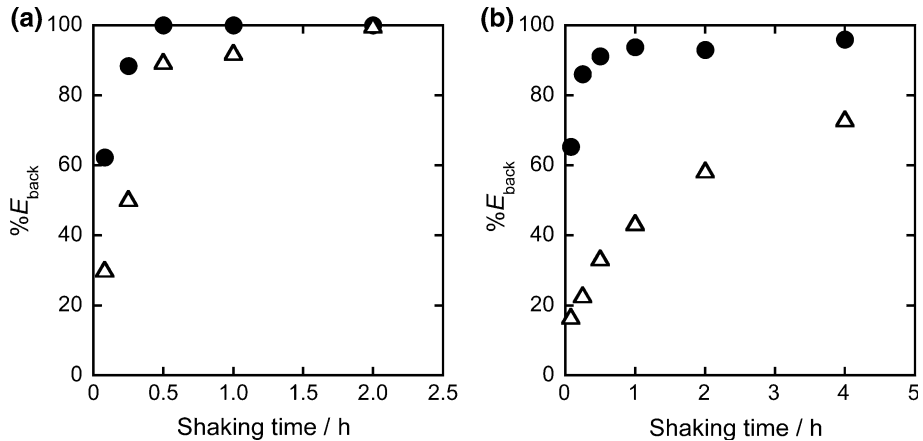


Fig. 4 Effect of shaking time on the back extraction percentages of Pd^{II} (filled circle) and Pt^{IV} (open triangle) from the IL phase ([HTOA][NO₃]) using a 1.0 mol-dm⁻³ aqueous HNO₃ solution containing thiourea. Initial metal concentration in the IL phase: 9.9×10^{-3} mol-dm⁻³ (Pd), 1.0×10^{-2} mol-dm⁻³ (Pt). IL/aqueous volume ratio: 1/10. Thiourea concentration: (a) 0.50 mol-dm⁻³ and (b) 0.10 mol-dm⁻³

volume ratio of 1/10. Figure 4a shows the plot of %E_{back} versus shaking time. Pd^{II} is quantitatively back-extracted with shaking time ≥ 30 min. In addition, the quantitative back extraction of Pt^{IV} is achieved by shaking for 2 h. The back extraction rate of Pt^{IV} is clearly slower than that of Pd^{II}. Then, the effect of the shaking time for back extraction was investigated again using an aqueous HNO₃ solution (1.0 mol-dm⁻³) containing more dilute thiourea (0.10 mol-dm⁻³), expecting the separation of Pd^{II} from Pt^{IV}. Figure 4b shows the result. The %E_{back} values are 86% for Pd^{II} and 23% for Pt^{IV} by shaking for 15 min and 91% for Pd^{II} and 34% for Pt^{IV} by shaking for 30 min. The mutual separation between Pd^{II} and Pt^{IV} by back extraction is not complete but possible to some extent.

3.4 Regeneration of [HTOA][NO₃]

During forward extraction, NO₃⁻ in the IL phase is partially exchanged with Cl⁻ as shown in Table 2. However, during back extraction using an aqueous thiourea solution containing HNO₃, Cl⁻ in the IL phase should be reexchanged with NO₃⁻. Therefore, [HTOA][NO₃] is expected to be regenerated by back extraction and reusable for the forward extraction of Pd^{II} and Pt^{IV}. To verify this, the following experiments were conducted. Assuming forward and back extraction, water-saturated [HTOA][NO₃] was shaken for 1 h at 25 °C with a 100-fold volume of 0.10 mol-dm⁻³ hydrochloric acid (not containing metals) and, after centrifugation, an aliquot of the IL phase was shaken for 2 h at 25 °C with a 10-fold volume of an aqueous solution containing 0.50 mol-dm⁻³ of thiourea and 1.0 mol-dm⁻³ of HNO₃. After centrifugation, the IL phase was used for the extraction of Pd^{II} or Pt^{IV} in a 100-fold volume of 0.10 mol-dm⁻³ hydrochloric acid. However, both metals were not well extracted, probably because of the presence of thiourea in the IL phase. Then, to remove thiourea, the IL phase was shaken with a 10-fold volume of an aqueous solution of 1.0 mol-dm⁻³ HNO₃ for 1 h. Using the IL phase after the scrubbing, 99% of Pd^{II} and 88% of Pt^{IV} were extracted during forward extraction from a 100-fold volume of a 0.10 mol-dm⁻³ hydrochloric acid solution. These %E values are nearly equal to those

obtained using fresh water-saturated [HTOA][NO₃] (Table 3), indicating the successful regeneration of [HTOA][NO₃].

4 Conclusion

At room temperature, water-saturated [HTOA][NO₃] is a liquid with a relatively low viscosity and sufficiently low aqueous solubility, which can be used as an extraction solvent without dilution. It has an extremely high extraction capability for Pd^{II} and Pt^{IV} in dilute hydrochloric acid, which is sufficient to quantitatively extract these metals from a 1000-fold volume of the aqueous phase. Other transition metals (Mn^{II}, Fe^{III}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, and Rh^{III}) are considerably less or marginally extracted into [HTOA][NO₃] from the dilute hydrochloric acid solution. The extraction capability of [HTOA][NO₃] is generally greater than those of the other hydrophobic ILs examined, such as [HTOA]Cl and several [NTf₂]⁻-based ILs. The metals extracted in the [HTOA][NO₃] phase are quantitatively back-extracted using an aqueous solution containing thiourea and HNO₃. By controlling the thiourea concentration and shaking time, the mutual separation of Pd^{II} and Pt^{IV} is also possible to some extent during back extraction. [HTOA][NO₃] can be readily, cost-effectively prepared by the neutralization of trioctylamine with nitric acid and can be regenerated via scrubbing the used IL with an aqueous HNO₃ solution. Consequently, this extraction system can be possibly applied for the industrial separation processes and preconcentration prior to the instrumental analysis of Pd^{II} and Pt^{IV}.

Acknowledgements The authors thank Ms. Sayaka Kado (Center for Analytical Instrumentation, Chiba University) for her technical support on mass spectrometry. The authors also thank Enago (www.enago.jp) for the English language review. This work was financially supported by JSPS KAKENHI Grant Number JP26410145.

References

1. PGM Market Report May 2017. Johnson Matthey Precious Metals Management, Royston (2017)
2. Fornalczyk, A., Saternus, M.: Removal of platinum group metals from the used auto catalytic converters. *Metalurgija* **48**, 133–136 (2009)
3. Bernardis, F.L., Grant, R.A., Sherrington, D.C.: A review of methods of separation of the platinum-group metals through their chloro-complexes. *React. Funct. Polym.* **65**, 205–217 (2005)
4. Cox, M.: Solvent extraction in hydrometallurgy. In: Rydberg, J., Cox, M., Musikas, C., Choppin, G.R. (eds.) *Solvent Extraction Principles and Practice*, 2nd edn, pp. 454–503. CRC/Taylor and Francis, Boca Raton (2004)
5. De Los Rios, A.P., Hernandez-Fernandez, F.J. (eds.): *Ionic Liquids in Separation Technology*. Elsevier, Amsterdam (2014)
6. Dai, S., Ju, Y.H., Barnes, C.E.: Solvent extraction of strontium nitrate by a crown ether using room-temperature ionic liquids. *J. Chem. Soc. Dalton Trans.* **1999**, 1201–1202 (1999)
7. Visser, A.E., Swatloski, R.P., Griffin, S.T., Hartman, D.H., Rogers, R.D.: Liquid/liquid extraction of metal ions in room temperature ionic liquids. *Sep. Sci. Technol.* **36**, 785–804 (2001)
8. Carda-Broch, S., Berthod, A., Armstrong, D.W.: Solvent properties of the 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid. *Anal. Bioanal. Chem.* **375**, 191–199 (2003)
9. Vidal, S.T.M., Correia, M.J.N., Marques, M.M., Ismael, M.R., Reis, M.T.A.: Studies on the use of ionic liquids as potential extractants of phenolic compounds and metal ions. *Sep. Sci. Technol.* **39**, 2155–2169 (2005)
10. Khachatryan, K.S., Smirnova, S.V., Torocheshnikova, I.I., Shvedene, N.V., Formanovsky, A.A., Pletnev, I.V.: Solvent extraction and extraction-voltammetric determination of phenols using room temperature ionic liquid. *Anal. Bioanal. Chem.* **381**, 464–470 (2005)

11. Vijayaraghavan, R., Vedaraman, N., Surianarayanan, M., MacFarlane, D.R.: Extraction and recovery of azo dyes into an ionic liquid. *Talanta* **69**, 1059–1062 (2006)
12. Pei, Y.C., Wang, J.J., Xuan, X.P., Fan, J., Fan, M.: Factors affecting ionic liquids based removal of anionic dyes from water. *Environ. Sci. Technol.* **41**, 5090–5095 (2007)
13. de los Rios, A.P., Hernandez-Fernandez, F.J., Lozano, L.J., Sanchez, S., Moreno, J.I., Godinez, C.: Removal of metal ions from aqueous solutions by extraction with ionic liquids. *J. Chem. Eng. Data* **55**, 605–608 (2010)
14. Katsuta, S., Nakamura, K., Kudo, Y., Takeda, Y., Kato, H.: Partition behavior of chlorophenols and nitrophenols between hydrophobic ionic liquids and water. *J. Chem. Eng. Data* **56**, 4083–4089 (2011)
15. Katsuta, S., Nakamura, K., Kudo, Y., Takeda, Y.: Mechanisms and rules of anion partition into ionic liquids: phenolate ions in ionic liquid/water biphasic systems. *J. Phys. Chem. B* **116**, 852–859 (2012)
16. Watanabe, Y., Katsuta, S.: Distribution of a monovalent anion in various ionic liquid/water biphasic systems: relationship of the distribution ratio of picrate ions with the aqueous solubility of ionic liquids. *J. Chem. Eng. Data* **59**, 696–701 (2014)
17. Katsuta, S., Watanabe, Y., Araki, Y., Kudo, Y.: Extraction of gold(III) from hydrochloric acid into various ionic liquids: relationship between extraction efficiency and aqueous solubility of ionic liquids. *ACS Sustain. Chem. Eng.* **4**, 564–571 (2016)
18. Hamamoto, T., Okai, M., Katsuta, S.: The laws governing ionic liquid extraction of cations: partition of 1-ethylpyridinium monocation and paraquat dication in ionic liquid/water biphasic systems. *J. Phys. Chem. B* **119**, 6317–6325 (2015)
19. Seeley, F.G., Crouse, D.J.: Extraction of metals from chloride solutions with amines. *J. Chem. Eng. Data* **11**, 424–429 (1966)
20. Galan, B., Urtiaga, A.M., Alonso, A.I., Irabien, J.A., Ortiz, M.I.: Extraction of anions with Aliquat 336: chemical equilibrium modeling. *Ind. Eng. Chem. Res.* **33**, 1765–1770 (1994)
21. Lee, M.-S., Lee, K.-J., Oh, Y.-J.: Solvent extraction equilibria of FeCl₃ from hydrochloric acid solution. *Mater. Trans.* **45**, 2364–2368 (2004)
22. Jha, M.K., Gupta, D., Lee, J.-C., Kumar, V., Jeong, J.: Solvent extraction of platinum using amine based extractants in different solutions: a review. *Hydrometallurgy* **142**, 60–69 (2014)
23. Cieszyńska, A., Wisniewski, M.: Extraction of palladium(II) from chloride solutions with Cyphos® IL 101/toluene mixtures as novel extractant. *Sep. Purif. Technol.* **73**, 202–207 (2010)
24. Wei, W., Cho, C.-W., Kim, S., Song, M.-H., Bediako, J.K., Yun, Y.-S.: Selective recovery of Au(III), Pt(IV), and Pd(II) from aqueous solutions by liquid–liquid extraction using ionic liquid Aliquat-336. *J. Mol. Liq.* **216**, 18–24 (2016)
25. Fontàs, C., Salvadó, V., Hidalgo, M.: Solvent extraction of Pt(IV) by Aliquat 336 and its application to a solid supported liquid membrane system. *Solvent Extr. Ion Exch.* **17**, 149–162 (1999)
26. Papaiconomou, N., Lee, J.-M., Salminen, J., von Stosch, M., Prausnitz, J.M.: Selective extraction of copper, mercury, silver, and palladium ions from water using hydrophobic ionic liquids. *Ind. Eng. Chem. Res.* **47**, 5080–5086 (2008)
27. Stojanovic, A., Kogelnig, D., Fischer, L., Hann, S., Galanski, M., Groessl, M., Krachler, R., Keppler, B.K.: Phosphonium and ammonium ionic liquids with aromatic anions: synthesis, properties, and platinum extraction. *Aust. J. Chem.* **63**, 511–524 (2010)
28. Katsuta, S., Yoshimoto, Y., Okai, M., Takeda, Y., Bessho, K.: Selective extraction of palladium and platinum from hydrochloric acid solutions by trioctylammonium-based mixed ionic liquids. *Ind. Eng. Chem. Res.* **50**, 12735–12740 (2011)
29. Génand-Pinaz, S., Papaiconomou, N., Leveque, J.-M.: Removal of platinum from water by precipitation or liquid–liquid extraction and separation from gold using ionic liquids. *Green Chem.* **15**, 2493–2501 (2013)
30. Yang, Y., Kubota, F., Baba, Y., Kamiya, N., Goto, M.: One step effective separation of platinum and palladium in an acidic chloride solution by using undiluted ionic liquids. *Solvent Extr. Res. Dev. Jpn.* **21**, 129–135 (2014)
31. Tong, Y., Wang, C., Huang, Y., Yang, Y.: Extraction and stripping of platinum from hydrochloric acid medium by mixed imidazolium ionic liquids. *Ind. Eng. Chem. Res.* **54**, 705–711 (2015)
32. Papaiconomou, N., Svecova, L., Bonnaud, C., Cathelin, L., Billard, I., Chainet, E.: Possibilities and limitations in separating Pt(IV) from Pd(II) combining imidazolium and phosphonium ionic liquids. *Dalton Trans.* **44**, 20131–20138 (2015)
33. Kasahara, I., Kanai, M., Taniguchi, M., Kakeba, A., Hata, N., Taguchi, S., Goto, K.: Bis[2-(5-bromo-2-pyridylazo)-5-(*N*-propyl-*N*-sulphopropylamino)phenolato]cobaltate(III) as a counter ion for the extraction and spectrophotometric determination of long-chain quaternary ammonium salts and tertiary alkylamines in the presence of each other. *Anal. Chim. Acta* **219**, 239–245 (1989)

34. Saito, G., Sugimoto, K., Hagino, K.: Spectrophotometric determination of nitrate and/or nitrite using brucine sulfate. *Bunseki Kagaku* **20**, 542–549 (1971)
35. Nakamura, K., Kudo, Y., Takeda, Y., Katsuta, S.: Partition of substituted benzenes between hydrophobic ionic liquids and water: evaluation of interactions between substituents and ionic liquids. *J. Chem. Eng. Data* **56**, 2160–2167 (2011)
36. Tokuda, H., Tsuzuki, S., Susan, M.A.B.H., Hayamizu, K., Watanabe, M.: How ionic are room-temperature ionic liquids? An indicator of the physicochemical properties. *J. Phys. Chem. B* **110**, 19593–19600 (2006)
37. Kakiuchi, T., Nishi, N.: Ionic liquid/water interface: a new electrified system for electrochemistry. *Electrochemistry* **74**, 942–948 (2006)
38. Riddick, J.A., Bunger, W.B., Sakano, T.K.: *Organic Solvents*, 4th edn. Wiley, New York (1986)
39. Högfeltdt, E. (ed.): *Stability Constants of Metal-Ion Complexes Part A: Inorganic Ligands*. Pergamon Press, Oxford (1982)
40. Kondo, K., Ourachi, T., Kaneiwa, T., Matsumoto, M.: Solvent extraction of precious metals with quaternary ammonium salts and its application to preparation of metal particles. *Solvent Extr. Res. Dev. Jpn.* **7**, 176–184 (2000)