

# Thermodynamic study of extraction behavior for precious metals using phosphonium-based ionic liquids

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## Abstract

In this study, several types of ILs consisting of triethyl-*n*-pentyl phosphonium; [P<sub>2225</sub><sup>+</sup>], triethyl-*n*-octyl phosphonium; [P<sub>2228</sub><sup>+</sup>], triethyl-*n*-dodecyl phosphonium; [P<sub>22212</sub><sup>+</sup>], and bis(trifluoromethylsulfonyl)amide; [NTf<sub>2</sub><sup>-</sup>] without extractant was applied for the solvent extraction of precious metals. The phosphonium-based ILs exhibited a high extractability for Au(III). The extraction mechanism would be considered as anion exchange reaction; [AuCl<sub>4</sub><sup>-</sup>]<sub>aq</sub> + [P<sub>2225</sub>][NTf<sub>2</sub>]<sub>IL</sub> ⇌ [P<sub>2225</sub>][AuCl<sub>4</sub>]<sub>IL</sub> + [NTf<sub>2</sub><sup>-</sup>]<sub>aq</sub>. Moreover, thermodynamic characteristics were evaluated at different operating temperatures. As a result, the Van't Hoff plot yielded a slope proportional to the enthalpy ( $\Delta H$ ) and the extraction reaction of Au(III) using [P<sub>222X</sub>][NTf<sub>2</sub>]<sub>IL</sub> (X=5,8,12) solely system was exothermic. According to Raman spectroscopic analysis of the extracted Au(III) complex, the [NTf<sub>2</sub><sup>-</sup>] anion would not be solvated around first coordination sphere at the centered Au<sup>3+</sup> cation.

In the case of Pt(IV) extraction using [P<sub>22212</sub>][NTf<sub>2</sub>]<sub>IL</sub> solely system, from the slope analysis, the extraction mechanism was also expressed as the anion exchange reaction: [PtCl<sub>6</sub><sup>2-</sup>]<sub>aq</sub> + 2[P<sub>22212</sub>][NTf<sub>2</sub>]<sub>IL</sub> ⇌ [P<sub>22212</sub>]<sub>2</sub>[PtCl<sub>6</sub>]<sub>IL</sub> + 2[NTf<sub>2</sub><sup>-</sup>]<sub>aq</sub>. According to the Van't Hoff plot, the enthalpy ( $\Delta H$ ) was also positive and the extraction reaction of Pt(IV) using [P<sub>22212</sub>][NTf<sub>2</sub>]<sub>IL</sub> solely system was exothermic. The related thermodynamic properties such as enthalpy and Gibbs free energy were also evaluated in this study.

## Keywords

Ionic liquids, Precious metals, Solvent extraction, Thermodynamics

## 1. Introduction

Ionic liquids (ILs) have been attracting research interest for their potential use in analytical field due to their unique property such as low melting point, high thermal stability, negligible vapor pressure and wide electrochemical window [1]. The most attractive advantage of ILs as a separation medium is negligible vapor pressure compared to conventional organic solvent. Many physicochemical properties of ILs can be controlled by the combination of cations and anions, which has led to the concept of ILs being “designer solvents” [2].

Au and Pt are important elements of the primary precious metals that still suffer from the lack of a viable modern separation process applicable to its purification. A number of research studies have been published recently aiming at the development of a solvent-based separation process. The extraction of precious metals by various ILs has been described in the literature [3-5]. Most of these investigations were focused on extraction mechanism and extracted metallic species. There are a few report on the temperature dependence of extraction reaction using IL solely system for precious metals. The temperature effect and the related thermodynamic analysis assisted the controlling the overpotential by electrodeposition after solvent extraction. Therefore, it is meaningful to develop a recovery process for precious metals by solvent extraction and direct electrodeposition. This process combined methods of IL extraction and electrodeposition was effective from the viewpoint of the elimination of multiple complex steps, low secondary wastes, and easy handling.

Recently, the characteristics of ILs with wide electrochemical window in conjunction with hydrophobicity were applied for the recovery of Cu [6], Sr [7], Pd [8-10] and U [11] by solvent extraction and direct electrodeposition. We also demonstrated that the recovery of Ru [12], Ir [13] and Pt [14-15] using phosphonium-based ILs by solvent extraction and direct electrodeposition was effective. In this study, we investigated the extraction mechanism of precious metals in phosphonium-based IL solely system. Then, the related thermodynamic analysis on the extraction reaction was also evaluated from the temperature dependence.

## 2. Experimental

### 2.1 Sample preparation

The IL triethyl-*n*-pentylphosphonium bis(trifluoromethyl-sulfonyl)amide, [P<sub>2225</sub>][NTf<sub>2</sub>], trioctyl-*n*-pentylphosphonium bis(trifluoromethyl-sulfonyl)amide, [P<sub>2228</sub>][NTf<sub>2</sub>], and tridodecyl-*n*-pentylphosphonium bis(trifluoromethyl-sulfonyl)amide [P<sub>22212</sub>][NTf<sub>2</sub>] were synthesized by the metathesis reaction of [P<sub>222X</sub>][Br], (X=5, 8, 12) (Nippon Chemical Industrial Co., Ltd., >99.5%) and Li[NTf<sub>2</sub>] (Kanto Chemical Co., Inc., 99.7%), as described previously [16]. The absence of a bromide anion in each IL was confirmed by using AgNO<sub>3</sub> after repeatedly washing the IL with distilled water. The obtained IL was dried under high vacuum

< -0.1 MPa at 393 K for more than 48 h.

## 2.2 Solvent extraction

[P<sub>222X</sub>][NTf<sub>2</sub>] (X=5, 8, 12) was applied as the functionality both extractant of precious metals and diluent. SX with the IL system was performed, where the extraction studies were carried out with a 1:1 IL to aqueous phase ratio. The operating temperature was changed from 298 K to 368 K. Stirring during the extraction process was performed at 350 rpm for 12 h. The extraction behavior of Au(III) as a function of variation of the [P<sub>222X</sub>][NTf<sub>2</sub>] (X=5, 8, 12) was studied to determine the stoichiometry of the extracted metal complex. The extraction behavior of Pt(IV) as a function of variation of the [P<sub>22212</sub>][NTf<sub>2</sub>] was also studied to determine the stoichiometry of the extracted metal complex. After equilibration, the concentration of the metallic species in the aqueous phase was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES, ICPE-9000, Shimadzu Co.). The distribution ratio (*D*) and the extraction efficiency (*E*) were calculated from the ICP-AES quantitative data according to Eq. (1).

$$D = \frac{[M]_{aq}^{ini} - [M]_{aq}^{fin}}{[M]_{aq}^{fin}}, \quad E(\%) = \frac{100D}{D + V_{aq}/V_{IL}} \quad (1)$$

Here, [*M*] and *V* represent the concentration of each metal ion and the volume, respectively. The subscripts 'aq' and 'IL' represent the aqueous and IL phases, respectively. The superscripts 'ini' and 'fin' represent the initial and final concentrations, respectively.

## 2.3 Raman spectroscopy

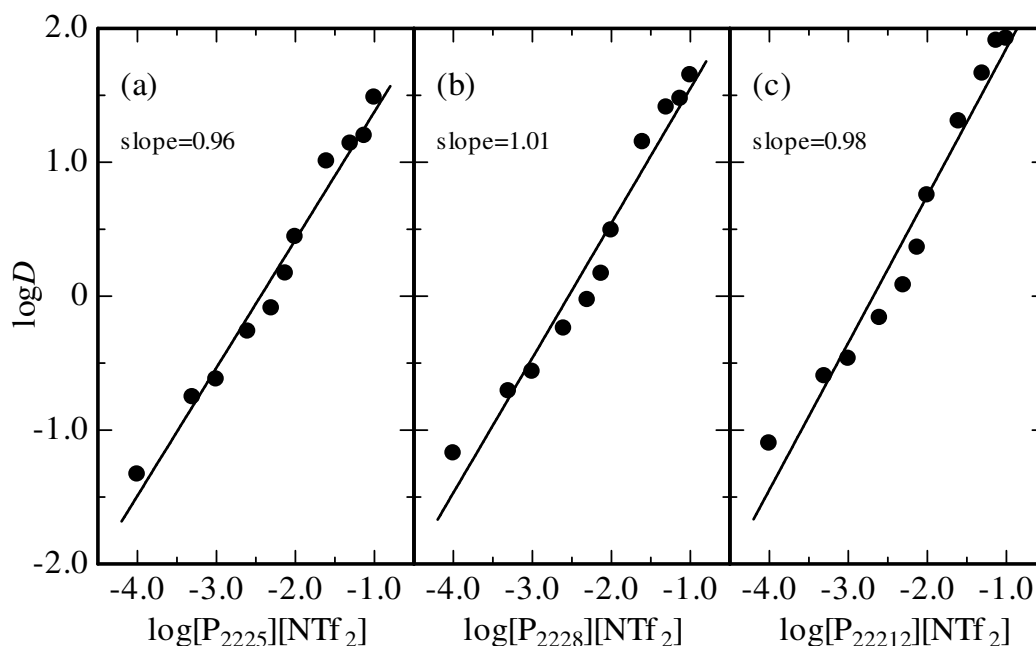
Raman spectra (inVia reflex, RENISHAW) were measured from 298 to 368 K using a 532-nm laser. The appropriate gratings for collecting the Raman spectra were 1800 mm<sup>-1</sup>. This condition was adopted to prevent fluorescence of the related ions, and this condition was selected based on the results of our recent investigations [17]. The concentration of the extracted Au(III) complex was determined from the extraction percentage after extraction equilibrium of [AuCl<sub>4</sub><sup>-</sup>] and [P<sub>2225</sub>][NTf<sub>2</sub>] solely system. The Raman spectra were measured by accumulating 512 individual measurements to improve the signal-to-noise ratio. The overlapping Raman bands were deconvoluted into individual components using a pseudo-Voigt function.

## 3. Results and discussion

### 3.1 Extraction mechanism of Au(III)

It is important to understand the stoichiometry of the extracted metal complex. The

extraction behavior of Au(III) with a change in the  $[P_{222X}][NTf_2]_{IL}$  ( $X=5, 8, 12$ ) concentration from  $1.0 \times 10^{-4}$  to  $1.0 \times 10^{-1}$  mol dm<sup>-3</sup> was shown in **Fig. 1**. The extraction result indicated that Au(III) was easily extracted by the anion exchange reaction in the  $[P_{222X}][NTf_2]_{IL}$  ( $X=5, 8, 12$ ) solely system. From the plot of  $\log D$  vs.  $\log[P_{222X}][NTf_2]_{IL}$  ( $X=5, 8, 12$ ), the respective slope of 0.96-1.01 indicated the association of one mole of the IL with one mole of  $[AuCl_4^-]$  during extraction. As a result,  $[P_{222X}][NTf_2]$  ( $X=5, 8, 12$ ) was an anion-exchange extractant for the extraction of Au(III) from chloride media in the form of anions.



**Fig. 1** Slope analysis of Au(III) with different types of phosphonium-based ILs.

(a)  $[P_{2225}][NTf_2]$ , (b)  $[P_{2228}][NTf_2]$  and (c)  $[P_{22212}][NTf_2]$

Thus, this type of phosphonium-based IL proceeded an anion-exchange reaction with Au(III) and the extraction mechanism for Au(III) with  $[P_{222X}][NTf_2]_{IL}$  ( $X=5, 8, 12$ ) can be expressed as follows.



The extraction equilibrium constant ( $K_{ex}$ ) and the distribution ratio ( $D$ ) are expressed as follows.

$$K_{ex} = \frac{[P_{222X}][AuCl_4]_{IL} [NTf_2]_{aq}}{[AuCl_4^-]_{aq} [P_{222X}][NTf_2]_{IL}}, \quad D = \frac{[P_{222X}][AuCl_4]_{IL}}{[AuCl_4^-]_{aq}} \quad (X=5,8,12) \quad (3)$$

The following relationship is obtained from Eq. (3).

$$K_{\text{ex}} = \frac{D[\text{NTf}_2]_{\text{aq}}}{[\text{P}_{222\text{X}}][\text{NTf}_2]_{\text{IL}}} \quad (\text{X}=5,8,12) \quad (4)$$

The logarithm of  $D$  is expressed as follows, according to the relation in Eq. (4):

$$\log D = \log K_{\text{ex}} - \log[\text{NTf}_2]_{\text{aq}} + \log[\text{P}_{222\text{X}}][\text{NTf}_2]_{\text{IL}} = \log K_{\text{ex}}' + \log[\text{P}_{222\text{X}}][\text{NTf}_2]_{\text{IL}} \quad (\text{X}=5,8,12) \quad (5)$$

where  $\log K_{\text{ex}}'$  is apparent equilibrium constant and evaluated from the intercept of  $\log[\text{P}_{222\text{X}}][\text{NTf}_2]_{\text{IL}}$  ( $\text{X}=5,8,12$ ) versus  $\log D$  as shown in **Fig. 1**. The calculated  $\log K_{\text{ex}}'$  for  $[\text{P}_{222\text{X}}][\text{NTf}_2]_{\text{IL}}$  ( $\text{X}=5,8,12$ ) was 2.332, 2.558 and 2.948, respectively. Although the viscosity of  $[\text{P}_{222\text{X}}][\text{NTf}_2]_{\text{IL}}$  ( $\text{X}=5,8,12$ ) became larger when the carbon number of alkyl side chain was increased, the value of  $\log K_{\text{ex}}'$  of  $[\text{P}_{22212}][\text{NTf}_2]_{\text{IL}}$  became higher than that of  $[\text{P}_{2225}][\text{NTf}_2]_{\text{IL}}$ . The result indicated that the bulk property would not be influenced on the extraction performance of Au(III).

In order to evaluate the thermodynamic parameters on the Au(III) extraction based on the following relation, the equilibrium constant ( $\log K_{\text{ex}}'$ ) were determined from the temperature dependence.

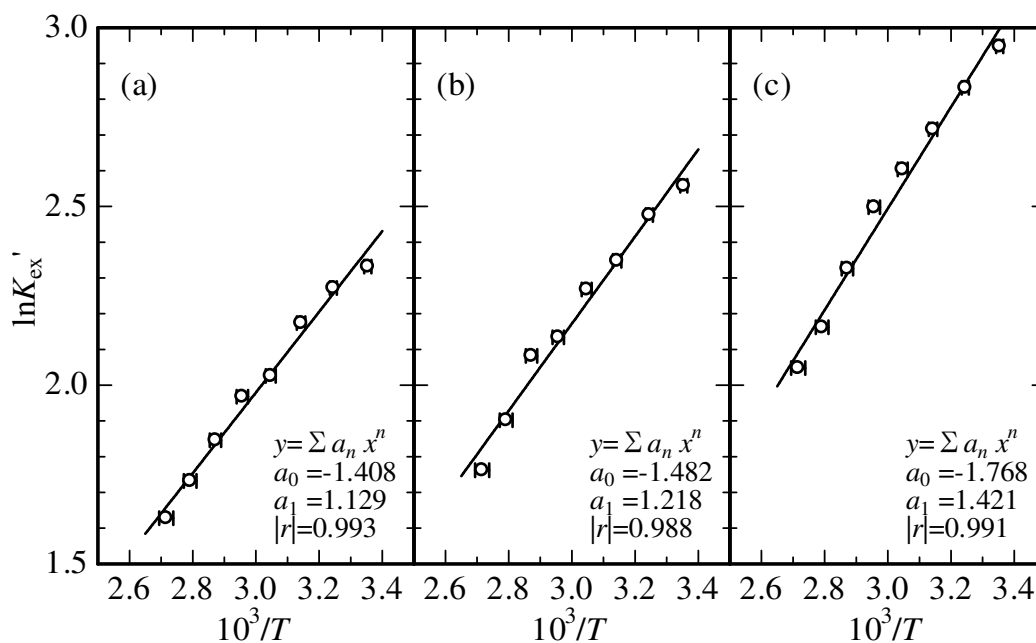
$$\Delta G = -RT \ln K_{\text{ex}}' = \Delta H - T\Delta S \quad (6)$$

The plot of the natural logarithm of  $K_{\text{ex}}'$  versus the inverse of the absolute temperature yields a slope proportional to the enthalpy ( $\Delta H$ )

$$\ln K_{\text{ex}}' = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (7)$$

By plotting  $T^{-1}$  versus  $\ln K_{\text{ex}}'$ , a line with a slope of 1.129-1.421 was obtained as shown in **Fig. 2**. Thus, the result indicated that the extraction reaction of Au(III) using  $[\text{P}_{222\text{X}}][\text{NTf}_2]_{\text{IL}}$  ( $\text{X}=5,8,12$ ) solely system was exothermic. The related thermodynamic properties were listed in **Table 1**. The negative value of  $T\Delta S$  indicated that the microscopic randomness was preferred in the  $[\text{P}_{2225}][\text{NTf}_2]_{\text{IL}}$  extraction system compared to  $[\text{P}_{22212}][\text{NTf}_2]_{\text{IL}}$ . Then,  $T\Delta S$  value on carbon number in alkyl side length would relatively be influenced on the total negative alternation in Gibbs energy on the extraction reaction, although the effectiveness of  $\Delta H$  was significantly affected on the total negative alternation in Gibbs energy. Thus, the tendency of the thermodynamic properties for Au(III) in  $[\text{P}_{222\text{X}}][\text{NTf}_2]_{\text{IL}}$  ( $\text{X}=5,8,12$ ) system

was similar to that in [C<sub>16</sub>mim]Cl system [18]. On the other hand, the separation factor of the related platinum group metals was tabulated in **Table 2**. [P<sub>2225</sub>][NTf<sub>2</sub>]<sub>IL</sub> and [P<sub>2228</sub>][NTf<sub>2</sub>]<sub>IL</sub> were found to be effective for the separation of Au/Pt and [P<sub>22212</sub>][NTf<sub>2</sub>]<sub>IL</sub> was desirable for the separation of Pt/Pd. Therefore, the extraction mechanism of Pt(IV) in [P<sub>22212</sub>][NTf<sub>2</sub>]<sub>IL</sub> solely system was further investigated in this study.



**Fig. 2** Van't Hoff plot of Au(III) with different types of phosphonium-based ILs.

(a) [P<sub>2225</sub>][NTf<sub>2</sub>], (b) [P<sub>2228</sub>][NTf<sub>2</sub>] and (c) [P<sub>22212</sub>][NTf<sub>2</sub>]

**Table 1** Thermodynamic parameter of extraction for Au(III) in phosphonium-based ILs.

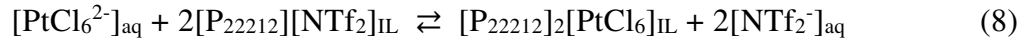
IL	$\Delta H/\text{kJ mol}^{-1}$	$T\Delta S/\text{kJ mol}^{-1}$	$\Delta G/\text{kJ mol}^{-1}$	$T/\text{K}$
[P <sub>2225</sub> ][NTf <sub>2</sub> ]	-9.39	-3.49	-5.90	298.15±0.80
[P <sub>2228</sub> ][NTf <sub>2</sub> ]	-10.13	-3.68	-6.45	
[P <sub>22212</sub> ][NTf <sub>2</sub> ]	-11.81	-4.38	-7.43	
[P <sub>2225</sub> ][NTf <sub>2</sub> ]	-9.39	-3.85	-5.55	328.15±0.84
[P <sub>2228</sub> ][NTf <sub>2</sub> ]	-10.13	-4.05	-6.08	
[P <sub>22212</sub> ][NTf <sub>2</sub> ]	-11.81	-4.83	-6.99	
[P <sub>2225</sub> ][NTf <sub>2</sub> ]	-9.39	-4.20	-5.19	358.15±0.96
[P <sub>2228</sub> ][NTf <sub>2</sub> ]	-10.13	-4.42	-5.71	
[P <sub>22212</sub> ][NTf <sub>2</sub> ]	-11.81	-5.27	-6.55	

**Table 2** Separation factor of PGM with different types of phosphonium-based ILs.

IL	$\beta(\text{Au/Pt})$	$\beta(\text{Pt/Pd})$	$\beta(\text{Pd/Ir})$	$\beta(\text{Ir/Ru})$
[P <sub>2225</sub> ][NTf <sub>2</sub> ]	26.45	1.38	0.46	2.03
[P <sub>2228</sub> ][NTf <sub>2</sub> ]	12.05	3.78	0.24	2.54
[P <sub>22212</sub> ][NTf <sub>2</sub> ]	0.12	19.53	1.83	9.15

### 3.2 Extraction mechanism of Pt(IV)

From the plot of  $\log D$  vs.  $\log[\text{P}_{22212}][\text{NTf}_2]_{\text{IL}}$  as shown in **Fig. 3(a)**, the respective slope of 1.85 indicated the association of two moles of the IL with one mole of  $[\text{PtCl}_6^{2-}]$  during extraction. As a result,  $[\text{P}_{22212}][\text{NTf}_2]$  was an anion-exchange extractant for the extraction of Pt(IV) from chloride media in the form of anions. This type of IL undergoes an anion-exchange reaction with Pt(IV) metal anion. Thus, the extraction mechanism for Pt(IV) with  $[\text{P}_{22212}][\text{NTf}_2]_{\text{IL}}$  can be expressed as follows.



The extraction equilibrium constant ( $K_{\text{ex}}$ ) and the distribution ratio ( $D$ ) are expressed as follows.

$$K_{\text{ex}} = \frac{[\text{P}_{22212}]_2[\text{PtCl}_6]_{\text{IL}}[\text{NTf}_2^-]_{\text{aq}}^2}{[\text{PtCl}_6^{2-}]_{\text{aq}}[\text{P}_{22212}][\text{NTf}_2]_{\text{IL}}^2}, \quad D = \frac{[\text{P}_{22212}]_2[\text{PtCl}_6]_{\text{IL}}}{[\text{PtCl}_6^{2-}]_{\text{aq}}} \quad (9)$$

The following relationship is obtained from Eq. (9).

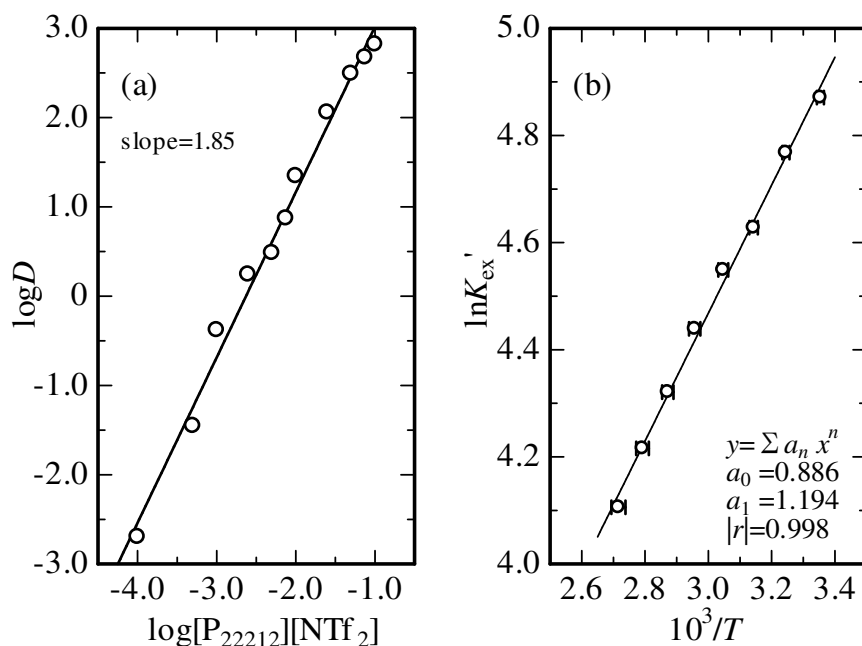
$$K_{\text{ex}} = \frac{D[\text{NTf}_2^-]_{\text{aq}}^2}{[\text{P}_{22212}][\text{NTf}_2]_{\text{IL}}^2} \quad (10)$$

The logarithm of  $D$  is expressed as follows, according to the relation in Eq. (10):

$$\log D = \log K_{\text{ex}} - 2\log[\text{NTf}_2^-]_{\text{aq}} + 2\log[\text{P}_{22212}][\text{NTf}_2]_{\text{IL}} = \log K_{\text{ex}}' + 2\log[\text{P}_{22212}][\text{NTf}_2]_{\text{IL}} \quad (11)$$

The extraction mechanism of Pt(IV) in  $[\text{P}_{222X}][\text{NTf}_2]_{\text{IL}}$  ( $X=5,8,12$ ) is also in good agreement with that in  $[\text{C}_{8\text{mim}}]\text{Cl}$  system [19,20]. In order to investigate the temperature dependence on the Pt(IV) extraction, the equilibrium constant ( $\log K_{\text{ex}}'$ ) and the thermodynamic parameters were evaluated from the change of operating temperatures. According to the Van't Hoff plot as shown in **Fig. 3(b)**, a line with a slope of 1.194 was obtained. Thus, the result indicated that the extraction reaction of Pt(IV) in  $[\text{P}_{22212}][\text{NTf}_2]_{\text{IL}}$  solely system was also exothermic.

The related thermodynamic properties were listed in **Table 3**. The negative value of  $T\Delta S$  with elevated temperature indicated that the microscopic randomness was preferred in the  $[P_{22212}][NTf_2]_{IL}$  extraction system. Then,  $T\Delta S$  value with elevated temperature would relatively be influenced on the total negative alternation in Gibbs energy on the extraction reaction, although the effectiveness of  $\Delta H$  was significantly affected on the total negative alternation in Gibbs energy.



**Fig. 3** (a) Slope analysis of Pt(IV) and (b) Van't Hoff plot using  $[P_{22212}][NTf_2]$  system.

**Table 3** Thermodynamic parameter of extraction for Pt(IV) on  $[P_{22212}][NTf_2]$  system.

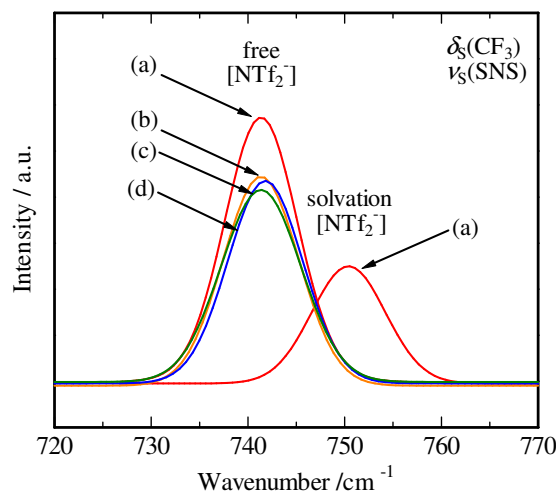
IL	$\Delta H/kJ\ mol^{-1}$	$T\Delta S/kJ\ mol^{-1}$	$\Delta G/kJ\ mol^{-1}$	$T/K$
$[P_{22212}][NTf_2]$	-9.93	-2.19	-12.12	$298.15 \pm 0.80$
		-2.41	-12.35	$328.15 \pm 0.84$
		-2.64	-12.57	$358.15 \pm 0.96$

### 3.3 Raman spectroscopic analysis

Raman spectrum of the extracted Au(III) in  $[P_{2225}][NTf_2]$  system was shown in **Fig. 4**. It is well known that the intense band at around  $740\ cm^{-1}$  in the Raman spectrum of the  $[NTf_2]^-$  anion in IL was assigned to the  $CF_3$  bending vibration  $\delta_s(CF_3)$  coupled with the S-N stretching vibration  $\nu_s(SNS)$  [21]. This intense band was attributed to free  $[NTf_2]^-$  anion, which did not coordinate with any metal cation. In the case of forming a solvation with a metal cation [22], this intense band shifts to around  $750\ cm^{-1}$ . For the extracted Au(III) sample, the intensity was



almost constant with increasing the operating temperature. However, no solvation  $[\text{NTf}_2^-]$  peak at  $750\text{ cm}^{-1}$  appeared for the extracted Au(III) sample. Consequently, the extracted Au(III) complex was  $[\text{P}_{2225}][\text{AuCl}_4]$  and  $[\text{NTf}_2^-]$  would not be solvated around first coordination sphere at the centered  $\text{Au}^{3+}$  cation. This result was consistent with the slope analysis of the  $[\text{NTf}_2^-]$  concentration.



**Fig. 4** Raman spectra of the extracted Au(III) complex in  $[\text{P}_{2225}][\text{NTf}_2]$  system.

(a) Solvated  $[\text{Nd}(\text{NTf}_2)_5]^{2-}$  in  $[\text{P}_{2225}][\text{NTf}_2]$  system (red line), (b) Au(III) in  $[\text{P}_{2225}][\text{NTf}_2]$  at 318 K (orange line), (c) Au(III) in  $[\text{P}_{2225}][\text{NTf}_2]$  at 338 K (green line) and (d) Au(III) in  $[\text{P}_{2225}][\text{NTf}_2]$  at 358 K (blue line)

#### 4. Conclusion

In this study, several types of ILs consisting of triethyl-*n*-pentyl phosphonium;  $[\text{P}_{2225}^+]$ , triethyl-*n*-octyl phosphonium;  $[\text{P}_{2228}^+]$ , triethyl-*n*-dodecyl phosphonium;  $[\text{P}_{22212}^+]$ , the other type of cations and bis(trifluoromethylsulfonyl)amide;  $[\text{NTf}_2^-]$  anion without extractant was applied for the solvent extraction of precious metals. The phosphonium-based ILs exhibited a high extractability for Au(III). The extraction mechanism would be considered as anion exchange reaction;  $[\text{AuCl}_4]_{\text{aq}} + [\text{P}_{2225}][\text{NTf}_2]_{\text{IL}} \rightleftharpoons [\text{P}_{2225}][\text{AuCl}_4]_{\text{IL}} + [\text{NTf}_2^-]_{\text{aq}}$ .

Moreover, thermodynamic characteristics were evaluated at different operating temperatures. As a result, the Van't Hoff plot yielded a slope proportional to the enthalpy ( $\Delta H$ ) and the extraction reaction of Au(III) using  $[\text{P}_{222X}][\text{NTf}_2]_{\text{IL}}$  ( $X=5,8,12$ ) solely system was exothermic. The tendency of the thermodynamic properties for Au(III) in  $[\text{P}_{222X}][\text{NTf}_2]_{\text{IL}}$  ( $X=5,8,12$ ) system was similar to that in  $[\text{C}_{16\text{mim}}]\text{Cl}$  system. According to Raman spectroscopic analysis of the extracted Au(III) complex, the  $[\text{NTf}_2^-]$  anion would not be solvated around first coordination sphere at the centered  $\text{Au}^{3+}$  cation.

In the case of Pt(IV) extraction using  $[\text{P}_{22212}][\text{NTf}_2]_{\text{IL}}$  solely system, from the slope

analysis, the extraction mechanism was also expressed as the anion exchange reaction:  $[\text{PtCl}_6^{2-}]_{\text{aq}} + 2[\text{P}_{22212}][\text{NTf}_2]_{\text{IL}} \rightleftharpoons [\text{P}_{22212}]_2[\text{PtCl}_6]_{\text{IL}} + 2[\text{NTf}_2^-]_{\text{aq}}$ . According to the Van't Hoff plot, the enthalpy ( $\Delta H$ ) was also negative and the extraction reaction of Pt(IV) using  $[\text{P}_{22212}][\text{NTf}_2]_{\text{IL}}$  solely system was exothermic. The related thermodynamic properties are also in good agreement with those in  $[\text{C}_{8\text{mim}}]\text{Cl}$  system.

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