

## **SOLVENT EXTRACTION OF PLATINUM(IV) FROM AQUEOUS ACIDIC CHLORIDE MEDIA WITH TRI-N-OCTYLAMINE IN TOLUENE**

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The extraction and stripping equilibria of platinum(IV) between acidic chloride media and tri-n-octylamine (TOA) in toluene were investigated at 303 K. Furthermore, the stripping of platinum(IV) with aqueous sodium hydroxide solution was also investigated. The experimental results are explained by a reversible reaction between the complex of TOA with hydrochloric acid and the hexachloro complex of platinum(IV),  $\text{PtCl}_6^{2-}$ , to form the complex  $(\text{TOA}\cdot\text{H})_2\text{PtCl}_6$  in toluene. At low TOA and high hydrochloric acid concentrations, the extracted platinum(IV) in toluene was quantitatively recovered by using aqueous hydrochloric acid solution. The extraction equilibrium constant was determined to be  $1.8 \times 10^6$ . The stripping of platinum(IV) with aqueous sodium hydroxide solution was easily performed. Complete stripping was achieved using an aqueous solution of sodium hydroxide, for which the molecular ratio to TOA-hydrochloric acid complexes was greater than unity.

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## 1. Introduction

Solvent extraction has been extensively studied in recent years and is a most important process for separation and purification of metals. In order to develop a solvent extraction process for precious metals from waste water or scrap, it is desirable to determine the fundamental aspects of the extraction equilibrium of metals with the extractant.

Separation and purification of platinum group metals by solvent extraction has been conducted using various types of extractants which have high selectivity for some individual elements of platinum group metals [1, 2]. However, only a few studies have been reported on the detailed quantitative analysis of the solvent extraction of platinum group metals and information on equilibrium constants is somewhat lacking. Further little information is available on stripping of Platinum group metals extracted into the organic phase.

Long-chain alkylamines have been known as useful extractants for extraction of the precious metals [3-7]. In our previous study, the extraction and stripping equilibria of palladium(II) with tri-n-octylamine (TOA) was examined to determine the complex type formed and the equilibrium constant [5]. In the present study, we have studied the solvent extraction of platinum(IV) with TOA from various concentrations of hydrochloric acid in aqueous solution. The purpose of this study is to determine the extraction equilibrium constant between platinum(IV) in aqueous hydrochloric acid solution and TOA in toluene. Furthermore, the stripping of the extracted platinum(IV) from toluene solution was investigated with aqueous hydrochloric acid solution and with aqueous sodium hydroxide solution, because the difficulty in stripping has become a problem in the application of this process [8].

## 2. Experimental

### 2.1 Reagents

TOA, (99.7%), kindly supplied from Koei Chemical Co., Ltd. was used as the extractant without further purification. Analytical grade hydrogen hexachloroplatinate(IV) hexahydrate was used as received for preparation of aqueous acidic solutions of platinum(IV) by dissolution in aqueous hydrochloric solutions of different concentrations. Reagent grade toluene was used as the organic diluent for preparation of organic solutions of TOA.

### 2.2 Procedure for Extraction of Platinum(IV)

The distribution equilibrium of platinum(IV) between aqueous acidic and organic solutions was measured batchwise as previously reported [5].

Equal volumes of TOA toluene solutions and aqueous solutions containing platinum(IV) salts, where each initial concentration was known, were shaken to attain

equilibrium in an Erlenmeyer flask immersed in a thermostatic water bath maintained at 303K. The initial platinum(IV) concentration in the aqueous solution was kept at  $0.5 \text{ mmol}\cdot\text{dm}^{-3}$  in this study. The concentration of TOA in toluene was measured by the same titration method as reported in our previous paper [9]. The platinum(IV) concentration in aqueous solution was determined by atomic absorption spectrophotometry.

The distribution coefficient,  $D$ , was defined as follows;

$$D = \frac{C_{\overline{\text{Pt}}}}{C_{\text{Pt}}} \quad (1)$$

where  $C_{\overline{\text{Pt}}}$  is the concentration of platinum(IV) extracted into the organic phase and  $C_{\text{Pt}}$  is that in the aqueous phase after equilibration.

The amount of platinum(IV) extracted into the organic solution was estimated by mass balance, since phase separation rapidly occurred, and the solubility of the organic solution in the aqueous phase and that of water in the organic phase were negligible. Further, the mass balance for platinum(IV) was checked by stripping the organic phase with aqueous NaOH solution and was found to be appropriate.

It has been suggested that equilibration of platinum(IV) extraction with TOA required a longer time than that of other precious metals, that is, palladium(II) and gold(III) from the results in the separation using microcapsules with encapsulated TOA [12]. Hence, the time required for equilibration in extraction and stripping of platinum(IV) was checked before the detailed study. It was found that the system reached equilibrium within  $14.4 \times 10^3 \text{ s}$ . Therefore, all subsequent experiments were run with overnight equilibration.

Reproducibility of the data was checked by carrying out the experiments several times.

### 2.3 Procedure for Stripping of Platinum(IV)

Toluene solutions of complexes between TOA and platinum(IV) (hereafter abbreviated as TOA-Pt(IV) complexes) were prepared by contacting a  $0.1 \text{ mol}\cdot\text{dm}^{-3}$  aqueous hydrochloric acid solution of  $1.0 \text{ mmol}\cdot\text{dm}^{-3}$  platinum(IV) with toluene solution containing various TOA concentrations at 303 K.

The stripping equilibria of platinum(IV) from the organic solution were studied using two different stripping solutions, that is, aqueous hydrochloric acid and aqueous NaOH solutions. Toluene solutions containing TOA-Pt(IV) complexes of various concentrations were contacted with stripping solution at 303 K. After phase separation, the concentration of Pt(IV) stripped into the aqueous solution was measured by atomic absorption spectrophotometry or induced coupled Argon plasma spectroscopy (ICAP). The definition of

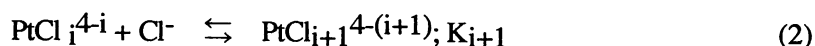
the distribution coefficient was the same as that for extraction (Equation (1)).

In the stripping experiments, the obtained data was shown to be reproducible by several trials.

### 3. Results and Discussion

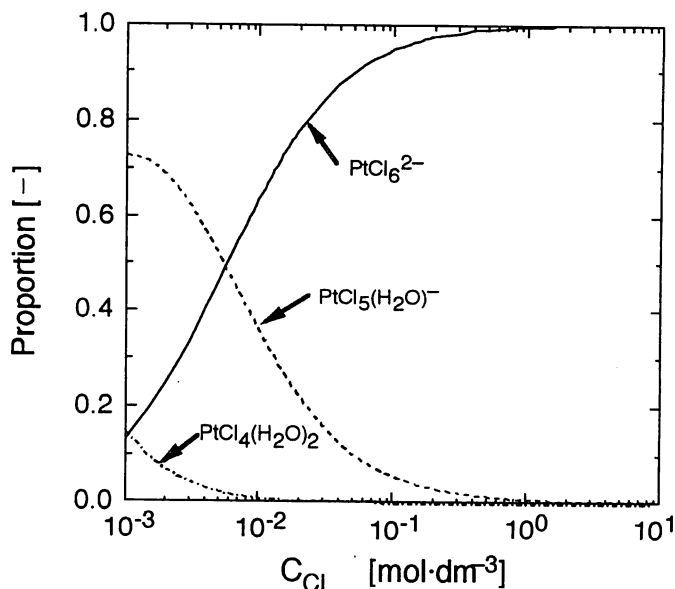
#### 3. 1 Proportion of Chloro-complexes of Platinum(IV)

It is well-known that platinum(IV) reacts with chloride ions to form chloro-complexes in aqueous chloride media. The complexation of platinum(IV) is expressed by the following equation.



$$K_{i+1} = \frac{C_{\text{PtCl}_{i+1}^{4-(i+1)}}}{C_{\text{PtCl}_i^{4-i}} \cdot C_{\text{Cl}^-}} \quad (3)$$

where  $K_{i+1}$  denotes the step wise stability constant of the  $i$ -th chloro-complex of platinum(IV). Assuming that only three types of chloro-complexes of platinum(IV) will exist in the aqueous acidic media in this study, that is, diaquatetrachloro complex,  $\text{PtCl}_4(\text{H}_2\text{O})_2$ , aquapentachloro complex,  $\text{PtCl}_5(\text{H}_2\text{O})^-$  and hexachloro complex,  $\text{PtCl}_6^{2-}$ , the variation in the proportions of the relevant chloro-complexes with chloride ion concentration is shown in Figure 1.



**Fig. 1** Proportion of chloro-complexes of Pt(IV) in chloride media

In this calculation, we used the following values as the stability constants of chloro-

complexes of platinum(IV):  $K_5 = 103.7$  and  $K_6 = 102.25$  [10]. As seen in Figure 1, we found that the dominant chloro-complex under the chloride ion concentration in the present study was  $\text{PtCl}_6^{2-}$ , while the proportions of  $\text{PtCl}_4(\text{H}_2\text{O})_2$  and  $\text{PtCl}_5(\text{H}_2\text{O})^-$  were negligible.

### 3.2 Extraction Equilibrium of Platinum(IV) with TOA

Solvent extraction of metals with long-chain alkylamines such as TOA is strongly dependent on the chloride concentration in the aqueous phase and the extractant concentration in the organic phase. The effects of the chloride and the extractant concentrations as the main parameters were investigated in detail.

The effect of initial TOA concentration on the distribution coefficient of platinum(IV) between the aqueous and organic solutions was examined for various hydrochloric acid concentrations. The results obtained are shown in Figure 2. It is obvious, from the figure, that the distribution coefficient of platinum(IV) increased with increasing TOA concentration depending on the hydrochloric acid concentration. The distribution coefficient with increasing hydrochloric acid concentration.

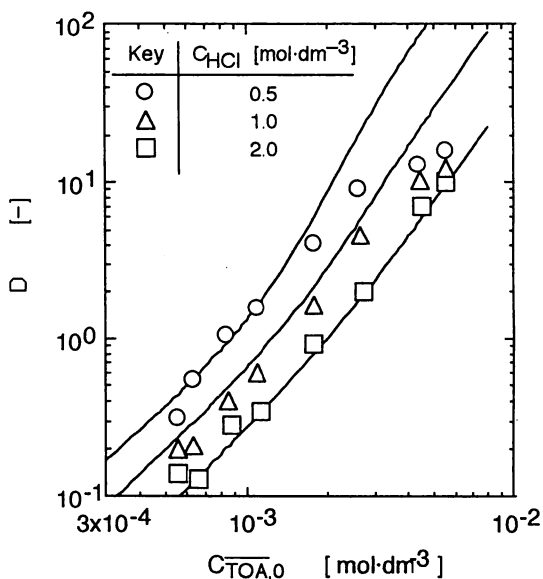
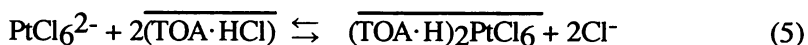


Fig. 2 Effect of initial TOA concentration on the distribution coefficient

At hydrochloric acid concentrations used in this study, it is known that all molecules of TOA react with hydrochloric acid to form a TOA-hydrochloric acid complex as follows [11]:



where  $\overline{\text{TOA} \cdot \text{HCl}}$  represents the complex between TOA and hydrochloric acid. The overbar refers to the organic phase. The extraction of platinum(IV) with TOA from aqueous hydrochloric acid media is expressed by the following equation:



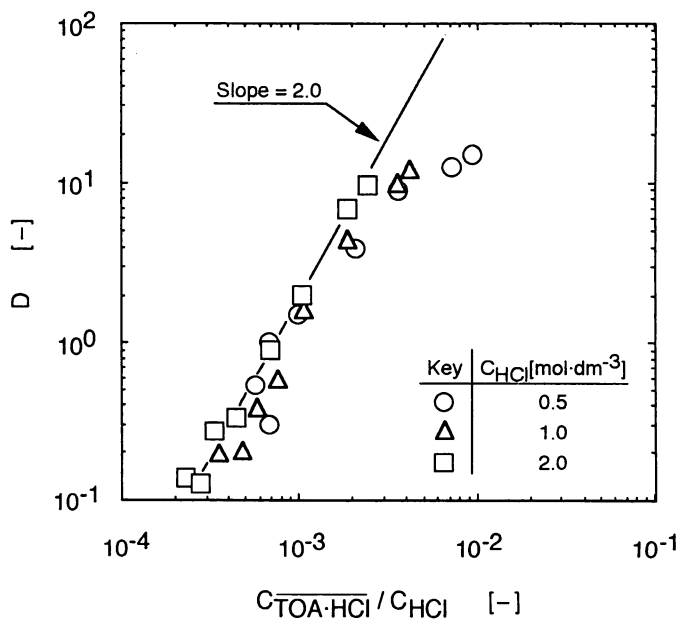
$$K_{\text{Pt}} = \frac{C_{\overline{(\text{TOA}\cdot\text{H})}_2\text{PtCl}_6} \cdot C_{\text{Cl}^-}^2}{C_{\text{PtCl}_6^{2-}} \cdot C_{\overline{\text{TOA}\cdot\text{HCl}}}^2} \quad (6)$$

where  $K_{\text{Pt}}$  is the equilibrium constant in Equation (5). From consideration of the distribution coefficient,  $D$ , Equation (6) can be rewritten as follows.

$$D = K_{\text{Pt}} \cdot \frac{C_{\overline{\text{TOA}\cdot\text{HCl}}}^2}{C_{\text{Cl}^-}^2} \quad (7)$$

In this equation, the concentration of free  $\overline{\text{TOA}\cdot\text{HCl}}$  can be estimated from the difference between the initial concentration of TOA and the equilibrium concentration of the extracted platinum(IV) from Equation (5).

Activities of respective chemical species should be adopted to discuss the extraction thermodynamics in detail. However, as the extraction equilibrations were carried out over a wide concentration range of relevant chemical species in this experiment, it is difficult to define activity coefficients of chemical species in such high concentration regions. Therefore, we used molar concentrations in the following section.



**Fig. 3** Plot of the extraction distribution coefficient against  $C_{\overline{\text{TOA}\cdot\text{HCl}}}/C_{\text{HCl}}$

The plots of the values of the extraction distribution coefficient against  $\frac{C_{\text{TOA}\cdot\text{HCl}}}{C_{\text{Cl}^-}}$  on a logarithmic scale are presented in Figure 3. All experimental data, except for the data at  $\frac{C_{\text{TOA}\cdot\text{HCl}}}{C_{\text{Cl}^-}}$  values higher than  $3 \times 10^{-3}$ , could be plotted on a straight line having a slope of 2.0. This result shows that the extraction of platinum(IV) with TOA is basically expressed by the reaction of Equation (5). The deviation at high  $\frac{C_{\text{TOA}\cdot\text{HCl}}}{C_{\text{Cl}^-}}$  in Figure 3 may be due to the formation of other extraction species. The extraction behavior at high concentration of TOA and low hydrochloric acid concentration is not still clear in detail. Further investigation of these conditions is necessary in future work.

The intercept of the straight line shown in Figure 3 gives the equilibrium constant, which was determined to be  $1.8 \times 10^6$  using all experimental results including the stripping work to be described later. The results calculated with the equilibrium constant are presented as the solid lines in Figure 2. The lines, except for the data at the highest TOA concentrations, agreed well with the experimental results.

### 3.3 Stripping Equilibrium of Platinum(IV)

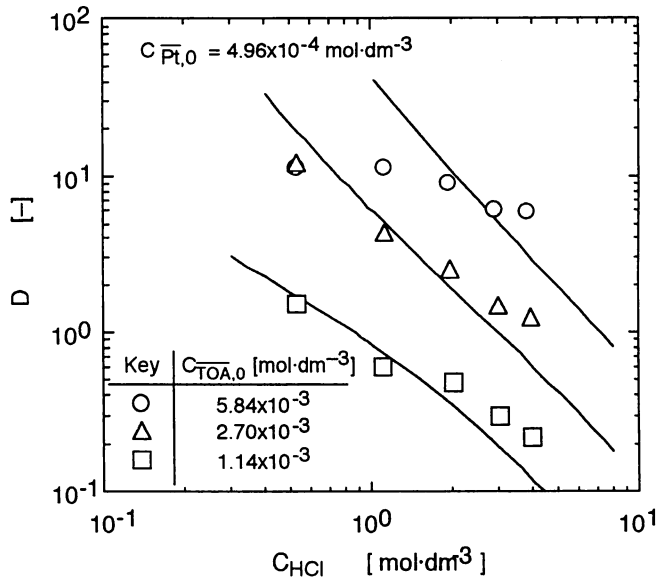
Stripping characterization is essential to construct the separation and concentration processes of various metals in aqueous solution by solvent extraction. In this system, the stripping mechanism has not been clarified yet, though TOA has been used in platinum(IV) extraction in many previous studies. In this study, two stripping solutions were adopted with different strategies. Stripping of platinum(IV) from the organic solution with aqueous hydrochloric acid is considered to proceed by breaking the ion pair, and stripping with an aqueous solution of sodium hydroxide is believed to proceed by deprotonating the complex between TOA and hydrochloric acid.

#### 3.3.1 Stripping with aqueous hydrochloric acid solution

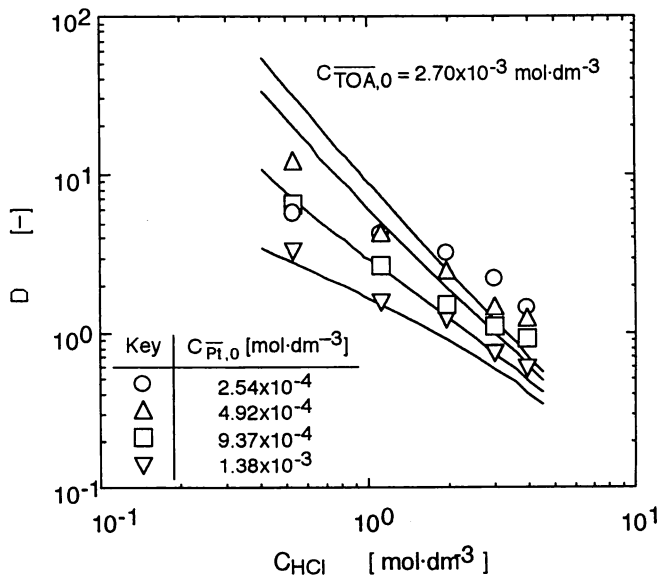
Figures 4 and 5 show the results of the stripping equilibrium with aqueous hydrochloric acid solution. As mentioned in the section on the extraction equilibrium, the distribution coefficient of platinum(IV) in the extraction was smaller than unity in regions of low TOA concentration and of high hydrochloric acid concentration. This suggested that stripping with aqueous hydrochloric acid solution could be established by adjusting the stripping conditions. Figure 4 represents the effect of hydrochloric acid concentration on the distribution coefficient of platinum(IV) for stripping at various concentrations of TOA. The TOA-Pt(IV) complex concentration was kept at  $0.5 \text{ mmol}\cdot\text{dm}^{-3}$ . As shown in this figure, the distribution coefficient of platinum(IV) in the stripping process decreased with increasing concentration of hydrochloric acid and increased with increasing TOA concentration. In particular, the distribution coefficient became smaller by using hydrochloric acid

concentrations greater than  $1.0 \text{ mol}\cdot\text{dm}^{-3}$  at  $1.14 \text{ mmol}\cdot\text{dm}^{-3}$  TOA. This result indicates that stripping of platinum(IV) is possible with aqueous hydrochloric acid solution in the TOA extraction system only at low TOA and high HCl concentrations. Figure 5 shows the effect of hydrochloric acid concentration on stripping at various initial concentrations of the TOA-Pt(IV) complex in the organic phase. The distribution coefficient was strongly affected by the TOA-Pt(IV) complex concentration and became smaller as the TOA-Pt(IV) complex concentration increased.

The results shown in Figures 4 and 5 indicated the possibility that the stripping proceeded following the backward reaction of Equation (5). Distribution coefficients in stripping were calculated by assuming that the stripping reaction was the reverse of the reaction in Equation (5) and that its equilibrium coefficient was  $1.8 \times 10^6$ . The calculated lines were represented in Figures 4



**Fig. 4** Effect of hydrochloric acid concentration in stripping solution on the distribution coefficient



**Fig. 5** Effect of extracted platinum(IV) concentration on the distribution coefficient in stripping



and 5 as solid lines. In the calculation, the concentration of free TOA·HCl was evaluated from the following relation.

$$\overline{C_{\text{TOA}\cdot\text{HCl}}} = \overline{C_{\text{TOA}\cdot\text{HCl},0}} - 2\overline{C_{\text{Pt},0}} + 2C_{\text{Pt}} \quad (8)$$

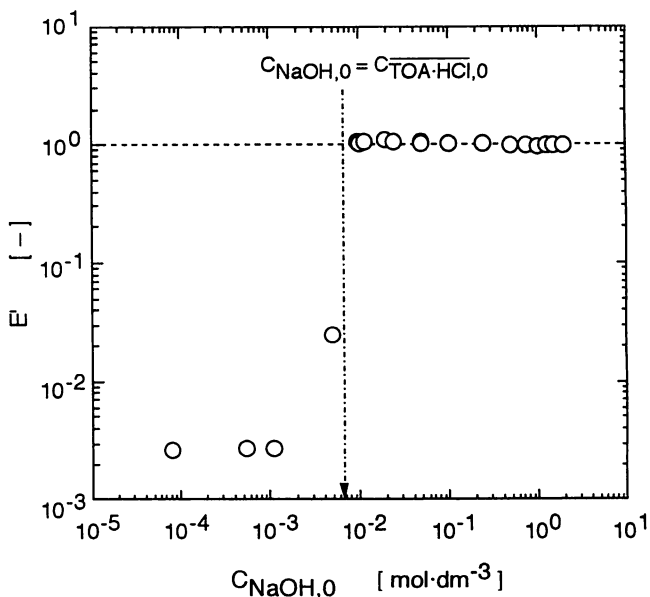
It was found, as can be seen in Figures 4 and 5, that the calculated lines satisfactorily expressed the stripping behavior and agreed with the experimental results.

### 3.3.2 Stripping with aqueous sodium hydroxide solution

Figure 6 shows the plots of the stripping ratio,  $E'$ , which is defined by Equation (9), against the sodium hydroxide concentration in the stripping solution.

$$E' = C_{\text{Pt}} / \overline{C_{\text{Pt},0}} \quad (9)$$

Platinum(IV) concentration in aqueous sodium hydroxide solution was measured by ICAP because of the strong interference between sodium and platinum(IV) in atomic absorption measurements. The platinum(IV) concentration extracted in the organic phase was adjusted to be about  $1.0 \text{ mmol}\cdot\text{dm}^{-3}$  and the initial concentration of TOA was  $6.27 \text{ mmol}\cdot\text{dm}^{-3}$ . It was obvious that the addition of sodium hydroxide in the stripping solution abruptly increased the stripping ratio of platinum(IV). The stripping ratio becomes constant and equal to unity above  $9.80 \text{ mmol}\cdot\text{dm}^{-3}$  of the sodium hydroxide concentration. Considering the obtained result and the equimolar concentration between sodium hydroxide and the TOA-hydrochloric acid complex which was  $6.27 \text{ mmol}\cdot\text{dm}^{-3}$  as shown in Figure 6, stripping with aqueous sodium hydroxide solution



**Fig. 6** Effect of sodium hydroxide concentration in aqueous solution on the stripping ratio

seems to proceed via deprotonation of TOA. That is, strong alkali reacts with TOA-hydrochloric acid complexes to form free TOA molecules which have no ability to extract metal ions from the aqueous phase.

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