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# The Separation of Platinum(II), Palladium(II) and Rhodium(III) by Surfactant Gel Extraction and an Abnormal Dependence of Metal Concentrations on the Extractability of Chloro-complexes into the Cationic Surfactant Phase

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A surfactant solution of cetylpyridinium chloride (CPC) separates into two phases by cooling the solution or by the addition of salts. Platinum(II) and palladium(II) react with chloride ions to form stable anionic complexes of $PtCl_4^{2-}$ and $PdCl_4^{2-}$, respectively, and were extracted into the CPC phase. Rhodium(III) does not form a chloro-complex and was separated from platinum(II) and palladium(II). CPC and its gel phase play the role of a counter ion and solvent for the anionic complexes. However, an abnormal decrease in extractability was observed for chloro-complexes at low metal concentrations and was explained by the solubility of complexes in the presence of the surfactant gel. A kinetic separation of palladium(II) from platinum(II) was performed by a ligand exchange reaction with ammonia. The cationic ammine complex of palladium(II) could not bind with the positively charged $CP^+$ and was back extracted into the aqueous phase. The platinum(II) chloro-complexes were stable for at least 3 hours below 50 °C and remained in the CPC phase.

## 1. Introduction

Recently, there has been a general concern for decreasing the discharge or disposal of effluents containing hazardous heavy metals. Such effluents often contain valuable metals; thus, there is an economic interest in their recovery for recycling. A variety of waste industrial products containing small amounts of precious metals are first leached in aqua regia, followed by classical chemical separation methods using liquid-liquid extraction, ion-exchange or precipitation.[1-7] The palladium and platinum metals are used as catalysts, electronic devices and ornamental metals. The purpose of this study is the separation and recovery of these metals with industrially important and widely used reagents such as chloride ion and ammonia. Rhodium, platinum and palladium are of interest in the purification of automotive exhaust gas as they are used in three way catalysts.[8]

Micellar solutions of ionic surfactants exhibit a phase separation on cooling the solutions below the Krafft point temperature (for CPC at 11°C)[9] or by the addition of a salt as a salting-out agent. Most of these surfactant phases are charged solids, which have the ability to bind oppositely charged complexes.[10] Surfactant extraction has been commonly used in studies for the extraction of ion-pair complexes, and in purification and pre-concentration of metals. In order to obtain high efficiency and selectivity, researchers use the formation of stable ionic complexes to remove metal ions from water. In the present study, the extractability of anionic chloro-complexes in the cationic surfactant solution was examined. We previously reported the direct extraction and/or adsorption of a metal ammine-complex into an anionic surfactant phase of sodium dodecylsulfate and the use of this process for the separation of copper(II) and zinc(II).[11,12]

An abnormal dependence of metal concentration on the extractability of complexes was observed in the extraction system relating to the cationic surfactant phase. This decrease in extractability affects the recovery process for metals in water.

## 2. Experimental

### 2-1. Reagents and solutions

Stock solutions, 1.00 x $10^{-2}$ mol $dm^{-3}$ of palladium(II), platinum(II)[2,13] and rhodium(III), were separately prepared by dissolving weighed amounts of palladium(II) chloride (Kanto Chemicals, Tokyo), potassium tetrachloroplatinate(II) (Kanto Chemicals, Tokyo) or rhodium(III) chloride trihydrate (Kanto Chemicals, Tokyo) in 4 $cm^3$ of concentrated hydrochloric acid and then diluting to 100 $cm^3$ with deionized water. The cationic surfactant, 0.25 mol $dm^{-3}$ of cetylpyridinium chloride (Tokyo Kasei, Tokyo), was prepared by dissolving this reagent in deionized water without further purification. The salting-out reagents, 2.0 mol $dm^{-3}$ of ammonium chloride (Kanto Chemicals, Tokyo), or a 2.0 mol $dm^{-3}$ of sodium chloride (Kanto Chemicals, Tokyo) solution, was prepared by dissolving these reagents in deionized water. A 5.0 mol $dm^{-3}$ of ammonia solution was prepared by diluting a concentrated ammonia solution (Kanto Chemicals, Tokyo). All other chemicals were of analytical grade and were dissolved in deionized water.

### 2-2. Apparatus

Absorbance measurements were performed using a Shimadzu UV-265 spectrophotometer with quartz cells of 1.0 cm path length. Metal concentrations were determined using a Varian Liberty Series II inductively coupled plasma atomic emission spectrometer (ICP-AES). All the pH measurements were performed using a Horiba F-11 pH meter in combination with a glass electrode. The concentration of CPC was determined by total organic carbon (TOC) measurements using a Shimadzu TOC-5000A. Heating of the solutions was carried out using a Buchi B-490 thermostatic bath. A Hitachi Himac CF7D2 centrifuge was used for phase separations.

### 2-3. Procedure

*Separation of palladium(II) and platinum(II) as chloro-complexes from rhodium(III).*

A solution containing platinum(II) and palladium(II), rhodium(III) was transferred to a 10 $cm^3$

centrifuge tube with a graduation line. After 1.0 $cm^3$ of 0.01 mol $dm^{-3}$ HCl and 1.0 $cm^3$ of 0.025 mol $dm^{-3}$ CPC were added, the solution was shaken to form the ion-pair. The salting out reagent, 2.5 $cm^3$ of 2.0 mol $dm^{-3}$ ammonium chloride or 2.5 $cm^3$ of 2.0 mol $dm^{-3}$ sodium chloride, was then added, and the mixture was diluted to 10 $cm^3$ with deionized water. After cooling the solution in an ice-water bath, the aqueous and CPC phases were separated by centrifugation (5000 rpm, 20 min, 0°C).

*Separation of the ammine complex of palladium(II) from platinum(II).*

After the removal of the aqueous phase which contained rhodium(III), a 2.0 $cm^3$ solution containing 5.0 mol $dm^{-3}$ ammonia was added to the CPC phase which was gel-like and located at the bottom of the centrifuge tube. The solution was diluted to 10 $cm^3$ with deionized water and heated for 10 min at 50°C. After cooling and centrifuging the solution, palladium(II) was recovered in the aqueous phase as the ammine complex, while platinum(II) remained in the CPC phase as the chloro-complex. After removal of the aqueous phase containing palladium(II), further ammonia solution was added to the CPC phase. Platinum(II) was recovered as the ammine complex in the aqueous phase by heating the solution for 30 min at 70°C.

## 3. Results and Discussion

### 3-1. Extraction of metal complexes into the CPC phase.

The reported stability constants (log $\beta_4$) are 13.8, 11.4, and 7.6 for $Pt^{II}Cl_4^{2-}$, $Pd^{II}Cl_4^{2-}$, and $Rh^{III}Cl_4^-$ in water, respectively.[14] Platinum(II) and palladium(II) formed stable complexes with chloride ions and extracted into the CPC phase via the following ion-pair formation reactions.

$$Pd^{2+} + 4Cl^- \rightleftharpoons PdCl_4^{2-} \qquad (1)$$

$$PdCl_4^{2-} + 2CP^+ \rightleftharpoons (PdCl_4^{2-})(CP^+)_2 \qquad (2)$$

$$Pt^{2+} + 4Cl^- \rightleftharpoons PtCl_4^{2-} \qquad (3)$$

$$PtCl_4^{2-} + 2CP^+ \rightleftharpoons (PtCl_4^{2-})(CP^+)_2 \qquad (4)$$

We previously reported the conditions for the extraction of these chloro-complexes[15], *i.e.*, between pH 1 and 5, NaCl or $NH_4Cl$ salting out agents at concentration of 0.1 to 2.0 mol $dm^{-3}$, and a CPC concentrations of 0.10 mmol $dm^{-3}$ to 0.10 mol $dm^{-3}$. The HCl concentration had no effect on the extraction between 0 to 1.0 mol $dm^{-3}$, because the salting out-agent provided a sufficient number of chloride ions. As seen from Fig. 1, the platinum(II) and palladium(II) chloro-complexes were quantitatively extracted over a wide ranges of metal concentrations and were easily separated from rhodium(III). However an unexpected decrease in extractabilities of the complexes was observed at low metal concentrations (Fig. 2). A similar decrease was reported for the extraction of cationic ammine complexes into the anionic surfactant phase and

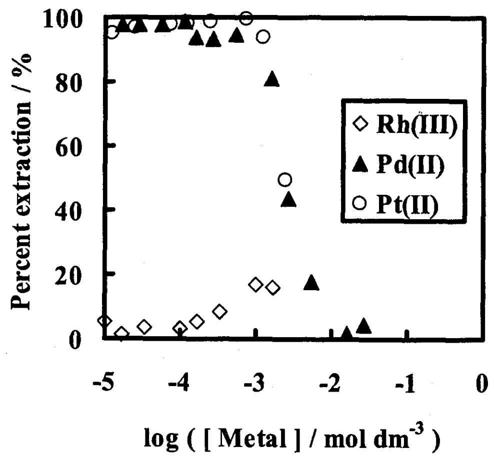

Fig. 1 Effect of metal concentration on the percent extraction. [HCl] = 1.0×$10^{-3}$ mol $dm^{-3}$, [CPC] = 2.5 × $10^{-3}$ mol $dm^{-3}$, [NaCl] = 0.50 mol $dm^{-3}$.

explained by the solubility product of the ion-pair[12].

We assumed that the extractability of the metals was affected by the solubility of the ion-pair formed in the aqueous phase. The solubility product of the ion-pair, $K_{SP}$, is defined as follows:

$$K_{SP} = [MCl_4^{2-}]_{aq}[CP^+]_{aq}^2 \qquad (5)$$

where $[MCl_4^{2-}]_{aq}$ and $[CP^+]_{aq}$ denote the equilibrium concentrations of the metal chloro-complex and cetylpyridinium cation in the aqueous phase, respectively. In the presence of the surfactant gel, the concentration of the CPC monomer ($[CP^+]_{aq}$ ) was independent of the initial surfactant concentration and was constant in the aqueous phase. Equation (5) is rewritten as eq.6

$$K_{SP} = \alpha^2[MCl_4^{2-}]_{aq} \qquad (6)$$

$$\alpha = (1.4\pm0.4)\times10^{-4}\ \mathrm{mol\ dm^{-3}} \qquad (7)$$

where α is the concentration of CPC which was determined by the TOC measurements in the aqueous phase. The equations related to the percent extraction and solubility product are

$$E(\%) = \{ 1 - ( [MCl_4^{2-}]_{aq} / [M]_{ini} ) \}\times100 \qquad (8)$$

$$E(\%) = \{ 1 - ( K_{SP} / \alpha^2[M]_{ini} ) \}\times100 \qquad (9)$$

The values of $K_{SP}$ were $2.7\times10^{-14}$ $(\mathrm{mol\ dm^{-3}})^3$ for Pd(II) and $3.4\times10^{-15}$ $(\mathrm{mol\ dm^{-3}})^3$ for Pt(II), respectively. The extraction curves calculated using equation (9) are shown as the solid lines in Fig. 2, and the percent extractions obtained experimentally are in good agreement with the theoretical curves.

### 3-2. Separation of palladium(II) from platinum(II) as ammine complex.

The separation and recovery of palladium and platinum is a common industrial process and it is based on a precipitation method.[5] The platinum(IV) complex, $PtCl_6^{2-}$, forms an insoluble precipitate with common inorganic cations such as potassium and ammonium ions, and $NH_4Cl$ is used as the recovery agent. However, in the presence of a large amount of $NH_4Cl$ as the salting out reagent, it has been difficult to separate the divalent ion complexes of

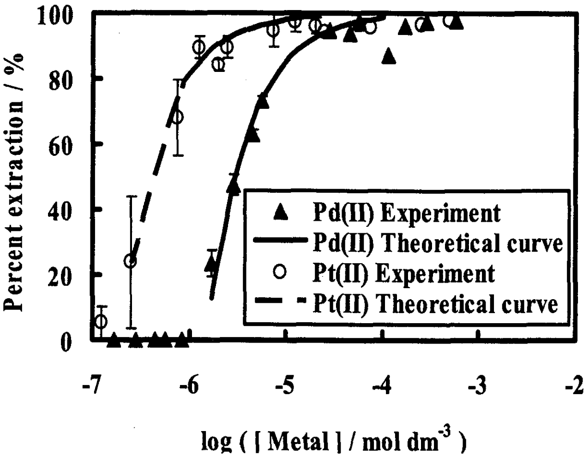

Fig. 2 Percent extraction at low metal concentrations. $[HCl] = 1.0\times10^{-3}$ mol dm$^{-3}$, $[CPC] = 2.5\times10^{-3}$ mol dm$^{-3}$, $[NaCl] = 0.50$ mol dm$^{-3}$. Percent extractions are given by the average values ( n = 4, α = 95% ).

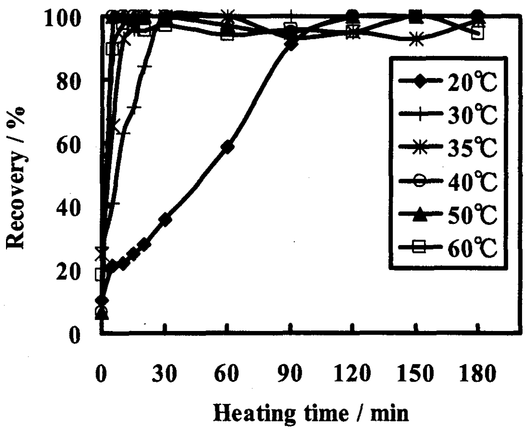

Fig. 3 Effect of heating time on the recovery of Pd(II).
$[Pd(II)] = 1.0\times10^{-4}$ mol dm$^{-3}$, $[CPC] = 2.5\times10^{-3}$ mol dm$^{-3}$, $[NaCl] = 0.50$ mol dm$^{-3}$, $[NH_3] = 1.0$ mol dm$^{-3}$.

platinum(II) and palladium(II). These complexes could not be precipitated with common cations in water. The separation of palladium(II) and platinum(II) was performed by the addition of ammonia during the back-extraction step. The ligand-exchange reaction of platinum(II) is very slow in aqueous solution[2,16], therefore a kinetic separation was examined using the Pd(II)-ammine complex. The platinum(II) chloro-complex was stable and remained in the CPC phase during the back-extraction step. On the other hand, as shown in Fig. 3, palladium(II) formed the Pd(II)-ammine complex by a ligand-exchange reaction and was back-extracted into the aqueous phase at 50°C within 3 min. The recovery of platinum(II) was achieved by heating the solution for 30 min at 70°C ( Fig. 4 ).

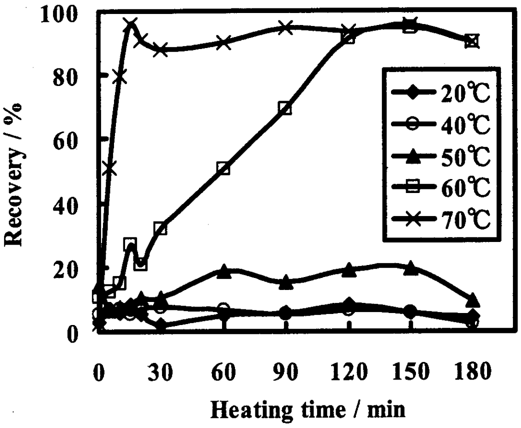

Fig. 4 Effect of heating time on the recovery of Pt(II).
[Pt(II)] = $1.0\times10^{-4}$ mol $dm^{-3}$, [CPC] = $2.5\times10^{-3}$ mol $dm^{-3}$, [NaCl] = 0.50 mol $dm^{-3}$, [$NH_3$] = 1.0 mol $dm^{-3}$.

Table 1 gives the separated recovery of palladium(II), platinum(II) and rhodium(III) in the mixed solution. The recovery of palladium(II) and platinum(II) was based on the formation of the ion-pair with the ionic surfactant and the extraction of the chloro-complexes into the surfactant phase. Though there is a limit to the recovery attributed to the specific solubility of the complexes in the ionic surfactant system, the surfactant-based separation processes have a significant potential as well as the traditional methods such as liquid-liquid extraction.

Table 1 Separation and recovery of the metals.

| **Procedure** | **Extraction** | **Back extraction 1 [a]** | **Back extraction 2 [b]** |
|---|---|---|---|
| **Metal** | **Rh(III)** | **Pd(II)** | **Pt(II)** |
| **Recovery / %** | **98.3 ± 0.9** | **93.1 ± 1.1** | **96.9 ± 1.2** |

Average ± SD ( 4 samples )
[a] Heating the solution for 10 min at 50°C.
[b] Heating the solution for 30 min at 70°C.

## 4. Conclusion

The chloro-complexes of metals formed ion-pairs with CPC and were extracted into the surfactant phase. After phase separation, the concentration of the CPC monomer was constant and low in the aqueous phase. A remarkable dependence of the metal concentration on the extractability was observed. The metal extractability was a function of the solubility of the ion-pair in the aqueous phase. Furthermore, palladium(II), platinum(II) and rhodium(III) were separated and recovered from the mixed solution. The present method will be available for the successive recovery of the major components in industrial and environmental samples and for the removal of the matrix in the pretreatment step for metal analyses.

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