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The Separation of Platinum(II) and Palladium(II) by Surfactant Gel Extraction (Part II)

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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) were reacted with chloride ions to form the stable complexes $PtCl_4^{2-}$ and $PdCl_4^{2-}$, respectively, and these were extracted into the CPC phase. The cationic surfactant CP^+ and the CPC gel play the role of a counter ion and an extraction solvent for these anionic complexes. A decrease in extractability was observed at low metal concentrations and applied to remove a large excess of palladium(II) from platinum(II) or that of platinum(II) from palladium(II) as the ion-pair $[PdCl_4^{2-}](CP^+)_2$ or $[PtCl_4^{2-}](CP^+)_2$. The percent extraction was (98.7±0.4) % and (6.4±7.3) % for 1.0×10^{-4} mol dm^{-3} palladium(II) and 3.0×10^{-7} mol dm^{-3} platinum(II), respectively. A small amount of metals remained in the aqueous phase after extraction. The pre-concentration of metals was performed by their extraction as electrically neutral complexes with pyrrolidinedithiocarbamate which gave a constant and complete extractability at low metal concentrations. By a combination of these extractions, it is possible to achieve successive separations of the major base metals from the minor components in the mixtures.

1. Introduction

Recently, there has been a general concern for reducing 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.[1-8] A variety of disposed industrial products containing small amounts of precious metals are first leached in aqua regia, followed by classical chemical separation methods using liquid-liquid extraction such as a multistage countercurrent extraction.[9] Many of the organic solvents are volatile and noxious, therefore new extraction media have been researched from the viewpoints of environmental protection and avoidance of harmful influence on human health.[10, 11]

Cationic surfactants are widely used in many applications such as cosmetics, hair rinses, industrial and commercial products. A separation process using surfactant gel properties has great potential for the removal of both inorganic and organic pollutants from water. These show a phase separation by the addition of a salt as a salting-out agent or by cooling the solutions below the Krafft point temperature. For example, this is 11℃ for CPC in water which could be changed by the conditions.[12] Most of these surfactant phases are charged solids, and they have the ability to bind an oppositely charged complex.[13] Surfactant extraction has been commonly used in studies for the extraction of ion-pair complexes and the purification and pre-concentration of metals.

Palladium and platinum are used as catalysts, in electronic devices and as ornamental metals. The separation and recovery of these metals are industrially important and have been used as catalysts in the purification of automotive exhaust gases.[14] We previously reported the extractability of anionic chloro-complexes of palladium(II) and platinum(II) in the CPC systems and the separation of these metals by the kinetic method.[15] The exchange reaction rate[2, 16] of palladium(II) between chloride and ammonia is fast comparing to that of platinum(II), and the cationic complex of [$Pd(NH_3)_4^{2+}$] formed was back-extracted into the aqueous phase after phase separation.

Separation methods based on the difference between reaction rates are sensitive to the experimental conditions such as initial metal concentrations, and are only applicable to samples which involved the same amounts of platinum(II) and palladium(II). Ammonium pyrrolidinedithiocarbamate (APDC) has been commonly used as a concentrating agent for many metals by solvent extraction and precipitation methods.[17] In the present study, the dependence of metal concentrations on the extractability of chloro-complexes was applied to the separation of metals and pre-concentration by extraction with PDC^- was used for the recovery process for metals in water. The separation of copper(II) was also examined because copper was one of the most common and important base metals.

2. Experimental

2-1. Reagents

The 1.00×10^{-2} mol dm^{-3} stock solutions of palladium(II), platinum(II)[2, 18] and copper(II) were separately prepared by dissolving weighed amounts of palladium(II) chloride (Kanto Chemicals, Tokyo), potassium tetrachloroplatinate(II) (Kanto Chemicals, Tokyo) and copper(II) chloride dihydrate (Kanto Chemicals, Tokyo) in 4.0 cm^3 of concentrated hydrochloric acid and then diluting to 100 cm^3 with deionized water. Working standards were prepared daily by appropriate dilution. The cationic surfactant, 0.25 mol dm^{-3} CPC (Tokyo Kasei, Tokyo), was prepared by dissolving this reagent in deionized water without further purification. The complexing agent, 5.0×10^{-2} mol dm^{-3} APDC (Kanto Chemicals, Tokyo), was prepared daily by dissolving this reagent in deionized water. The salting-out reagent, 2.0 mol dm^{-3} NaCl (Kanto Chemicals, Tokyo), was prepared by dissolving this reagent in deionized water. All other chemicals were of analytical grade and were dissolved in deionized water.

2-2. Apparatus

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 CP^+ was determined by Total Organic Carbon (TOC) measurement 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 copper(II).

A solution containing platinum(II), palladium(II) and copper(II) 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} NaCl, was then added, and the mixture was diluted to 10 cm^3 with deionized water. After cooling the solution in an ice-water bath and centrifuging (5000 rpm, 20 min, 0℃), the aqueous and CPC phases were separated. The metal concentrations were measured by ICP-AES in the aqueous phase, and at low metal concentrations below the detection limit, preconcentration was performed by heating and evaporation of the aqueous phase after phase separation in the 50 cm^3 centrifuge tube.

Pre-concentration of palladium(II), platinum(II) and copper(II) as the PDC-complex.

A solution containing platinum(II), palladium(II) and copper(II) was transferred to a 10 cm^3 centrifuge tube with a graduation line. After 1.0 cm^3 of 0.25 mol dm^{-3} CPC and 1.0 cm^3 APDC were added, the solution was shaken to form the ion-pair. The salting out reagent, 2.5 cm^3 of NaCl, was then added, and the mixture was diluted to 10 cm^3 with deionized water. After cooling and centrifuging, the CPC phase containing the concentrated metals was obtained.

Decomposition of PDC- complex.

After the removal of the aqueous phase, 5.0 cm^3 of 1.0 mol dm^{-3} HCl was added to the CPC phase which was gel-like and located at the bottom of the centrifuge tube. The solution was then diluted to 10 cm^3 with deionized water and heated for 30 min at 90℃. After cooling and centrifuging the solution, copper(II) was recovered into the aqueous phase, while palladium(II) and platinum(II) remained in the CPC phase.

3. Results and Discussion

3-1. Extraction of metals as chloro-complexes into the CPC phase.

We previously reported that a decrease of extractabilities of complexes was observed at low metal concentrations.[15] This decrease was explained by the unique solubility product of ion-pairs. In the presence of the surfactant gel, the concentration of CPC monomer ($[CP^+]_{aq}$) was independent of the initial surfactant concentration and was constant in the aqueous phase. The solubility product of the ion-pair, K_{SP}, is defined as follows:

$$K_{SP} = [MCl_4^{2-}]_{aq}[CP^+]_{aq}^2 \qquad (1)$$

where $[MCl_4^{2-}]_{aq}$ denotes the equilibrium concentrations of the metal chloro-complexes. The concentration of the surfactant monomer ($[CP^+]_{aq}$) was obtained by TOC measurement in the aqueous phase. The equations related to the percent extraction, E(%), and solubility product are

$$E(\%) = \{\ 1 - (\ K_{SP} / [CP^+]_{aq}^2[M]_{ini}\ )\ \}\times 100 \qquad (2)$$

and the values of -log K_{SP} were 13.6 $(mol\ dm^{-3})^3$ for palladium(II) and 14.5 $(mol\ dm^{-3})^3$ for platinum(II), respectively. However, these values were obtained using individual solutions contained only one metal. The question remained that metal ions were co-precipitated in the mixed solution which involved more than two metal ions. In Fig. 1, the concentration of palladium(II) was fixed at a large excess and the concentration of platinum(II) was variously changed and vice versa. The values of -log K_{SP} obtained were 13.8±0.1 (mol dm^{-3})^3 for palladium(II) and 14.2±0.6 (mol dm^{-3})^3 for platinum(II), respectively. The values obtained in the mixed solutions were in good agreement with the previous ones. This result suggested that the extraction system using surfactant media will not cause co-precipitation or co-extraction, and independently extracts the metals. As shown in Table 1, the separation was examined for 1.0×10^{-4} mol dm^{-3} palladium(II) and 3.0×10^{-7} mol dm^{-3} platinum(II) and only palladium(II) was extracted into the CPC phase. Platinum(II) at low concentration was not extracted and remained in the aqueous phase. The same result was obtained for a large excess of platinum(II).

3-2. Pre-concentration of palladium(II), platinum(II) and copper(II) as PDC-complexes.

The metal concentrations of 9.1×10^{-7} mol dm^{-3} palladium(II) and 3.0×10^{-7} mol dm^{-3} platinum(II) were calculated by eq. 2 at E(%) = 0. The added base metal, copper(II), was not extracted and remained in the aqueous phase because copper(II) could not form a chloro-complex. In order to maintain the successive extraction, we examined pre-concentration using APDC. Optimal extraction conditions were as follows: CPC concentration from 0.02 mol dm^{-3} to 0.10 mol dm^{-3}, APDC concentration from 0.5×10^{-3} mol dm^{-3} to 0.01 mol dm^{-3}, and the salting out agent, NaCl, from 0.2 to 1.0 mol dm^{-3}. As shown Fig. 2, palladium(II), platinum(II) and copper(II) formed stable complexes with APDC between pH 2 and 12 and

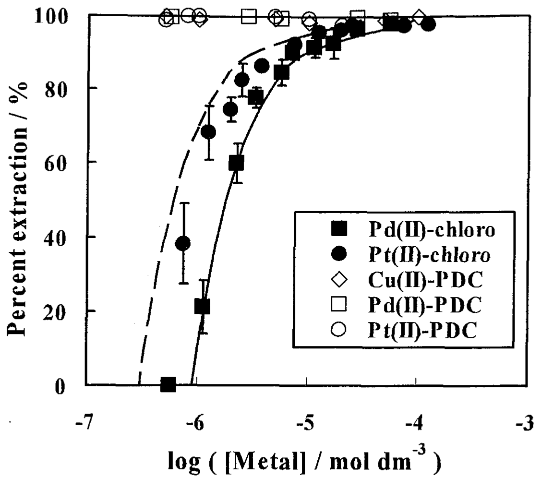


Fig. 1 Percent extraction as metal-chloro and metal-PDC complexes. [NaCl] = 0.50 mol dm^{-3}. ■: [Pt(II)] = 1.0×10^{-4} mol dm^{-3}, [HCl] = 1.0×10^{-3} mol dm^{-3}, [CPC] = 2.5×10^{-3} mol dm^{-3}. ●: [Pd(II)] = 1.0×10^{-4} mol dm^{-3}. Percent extractions are given by the average values (n=4, α=95%).◇, □, ○: [CPC] = 2.5×10^{-2} mol dm^{-3}, [APDC] = 5.0×10^{-3} mol dm^{-3}.

Table 1 Percent extraction of metals in the mixed solution.

Metals	Percent extraction / %
[Pd(II)] = 1×10^{-4} mol dm^{-3}	98.7 ± 0.4
[Pt(II)] = 3×10^{-7} mol dm^{-3}	6.4 ± 7.3

Metals	Percent extraction / %
[Pt(II)] = 1×10^{-4} mol dm^{-3}	98.5 ± 0.5
[Pd(II)] = 3×10^{-7} mol dm^{-3}	3.6 ± 4.1

Average values ± S.D. (n = 8 samples)

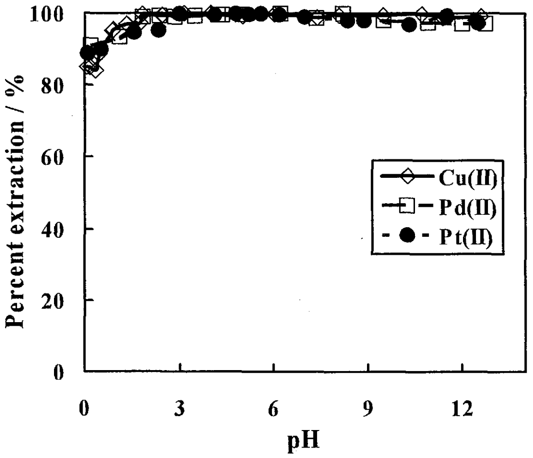
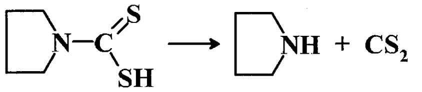


Fig. 2 Effect of pH on the percent extraction. [Metal] = 1.0×10^{-5} mol dm^{-3}, [CPC] = 2.5×10^{-2} mol dm^{-3}, [APDC] = 5.0×10^{-3} mol dm^{-3}, [NaCl] = 0.50 mol dm^{-3}.

could be readily extracted into the CPC phase. At pH 2, percent extractions of these metals decreased, because the acidic form of dithiocarbamate was unstable and decomposed in the acidic micellar solution.[19]



(3)

The complexes of platinum(II), palladium(II) and copper(II)-PDC were quantitatively extracted over a wide range and no decrease in the percent extraction was observed at low metal concentrations (Fig. 1).

3-3. Decomposition of the PDC-complex and recover of metals into the aqueous phase.

The separation of palladium(II) and platinum(II) from copper(II) was performed by the back-extraction method. The decomposition of the PDC-complexes was performed by the addition of HCl and heating the solution. The copper(II) complex was immediately decomposed and back-extracted into the aqueous phase. The platinum(II) and palladium(II) remained in the CPC phase during the back-extraction step. The stability of the PDC-complexes of palladium(II) and platinum(II) had no influence on the extractability, because the metal ions (M^{2+}) which were formed by the decomposition of the PDC-complexes gave anionic complexes with chloride anions and also were extracted into the CPC phase. The separation of $[PdCl_4^{2-}](CP^+)_2$ and $[PtCl_4^{2-}](CP^+)_2$ can be achieved by the addition of ammonia during the back-extraction step which was previously reported after pre-concentration.[15]

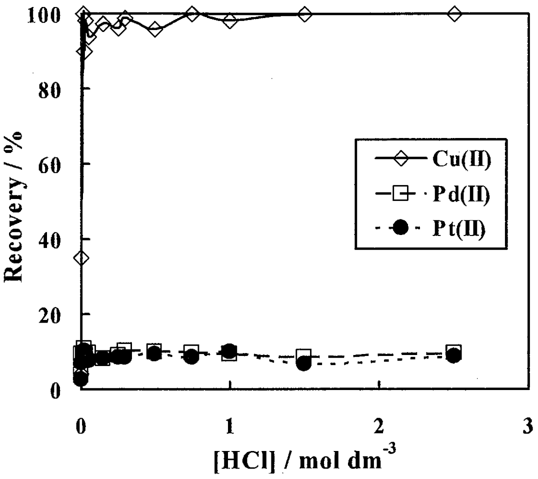


Fig. 3 Effect of HCl concentration on the recovery of metals. [Metal] = 1.0×10^{-5} mol dm^{-3}, [CPC] = 2.5×10^{-2} mol dm^{-3}, [APDC] = 5.0×10^{-3} mol dm^{-3}, [NaCl] = 0.50 mol dm^{-3}. Heating solutions for 30 min at 90℃.

4. Conclusion

A remarkable dependence of metal concentration on extractability was observed in the mixed solution. There was no co-precipitation or co-extraction. Optimal conditions for the pre-concentration method with using APDC were determined. By combination of two extraction methods, successive separation and recover of the major components from the minor can be obtained in the industrial and environmental samples and the removal of matrix metals for the pretreatment of analyses.

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