

# The ion-pair formation between dodecylsulfate and ammine-complexes of copper(II), nickel(II), zinc(II), palladium(II) and platinum(II), and the extraction behavior of the ammine-complexes by using sodium dodecylsulfate

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## Abstract

A micellar solution of sodium dodecylsulfate (SDS) exhibits the property of being separated into two phases due to a temperature change or the addition of salts. The ammine-complexes of copper(II), nickel(II) and palladium(II) reacted with the dodecylsulfate anion to form the corresponding ion-pair, and were extracted into the SDS gel phase. The SDS plays the roles of a pairing-ion for the ammine-complexes and of an extraction medium. The ion-pair extraction mechanism was investigated; the extractability of metals was given by the function of the solubility products of the ion-pairs. This method was applied to the mutual separation of Ni(II)/Cu(II) and Pd(II)/Pt(II). The driving force for the extraction was an electrostatic interaction between the cationic complex and the surfactant anion. The use of the SDS gel as ion-exchanger is also expected.

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**Keywords:** Ammine-complex; Dodecylsulfate anion; Solubility of ion-pairs; Ion-exchange

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## 1. Introduction

Interest has been shown in the separation of metal ions by an extraction and/or adsorption method that uses a surfactant and a polymer electrolyte of a solid or a liquid as the extraction medium [1–7].

In the method using the surfactant, the cloud point phenomenon has been commonly used in the science of the separation for extraction, purification and preconcentration of metals. It is based on the behavior of non-ionic surfactant aqueous solutions that exhibit a phase separation by increasing the temperature [8–16]. On the other hand, ionic surfactants show a phase separation by cooling the solutions below the Krafft point temperature. The analytical utility of these separation techniques is still limited and a few methods were

reported concerning the formation of ion-pairs and the extraction into the surfactant phase that is gel-like and has a lamellar structure. The exact mechanism has not yet been clarified for the ionic surfactant systems because the ion-pair formation affects the structure of the separated surfactant, phase and changes the extractability of the metals [17,18].

Recently, there has been 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. Ammonia is an important substance because it has a large number of utilizations for the industrial recovery of metals. For example, it is used as a leaching reagent for copper from chalcocite or chalcopyrite in the mining industry [19] and for the recovery of copper from spent etching agents [20]. However, there are only a few reports concerning the direct extraction of a metal as an ammine-complex. In the conventional liquid–liquid extractions, the ammine-complex

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undergoes a ligand exchange reaction using a hydrophobic reagent, such as LIX-973N [21]. Solvent extraction is then carried out [1,2,21]. Many of the organic solvents used are volatile and noxious [21]; therefore, the solvent extraction methods are not desirable from the viewpoint of environmental preservation and their harmful influence on human health. Moreover, the exchange reaction using hydrophobic reagents has the disadvantage of high cost and is time-consuming.

The purpose of this study is the direct extraction of a metal ammine-complex into an ionic surfactant phase and the clarification of the extraction mechanism of the ion-pair. Many divalent metals, such as copper(II), nickel(II), zinc(II), palladium(II) and platinum(II), form stable complexes with ammonia in aqueous solution. These complexes have a positive charge and several of them form an ion-pair with the anionic surfactants. Sodium dodecylsulfate (SDS) was selected because a micellar solution of this surfactant exhibits the property of being separated into two phases by cooling below the Krafft point temperature of 9 °C in pure water [22] or the addition of a salt. One is a surfactant-depleted phase (aqueous phase) and the other is a surfactant-rich phase known as the surfactant phase. SDS is used in household detergents, and has the advantage of low toxicity and high biodegradability. The metal complexes of copper(II), nickel(II) and palladium(II) form a water-insoluble ion-pair with the dodecylsulfate anion ( $\text{DS}^-$ ). The extractability of their metals depends on the metal concentrations and is almost independent of the SDS concentrations. Based on the solubility of an ion-pair in the aqueous phase, the mutual separation of metals was performed.

## 2. Experimental

### 2.1. Reagents

The stock solutions of divalent metal ions were separately prepared by dissolving the appropriate amounts of copper(II) nitrate (Kishida Chemicals, Osaka, Japan), nickel(II) nitrate (Wako Pure Chemicals, Tokyo, Japan), zinc(II) nitrate (Kishida Chemicals, Osaka, Japan), palladium(II) chloride (Kanto Chemicals, Tokyo, Japan), and potassium tetrachloroplatinate(II) (Kanto Chemicals, Tokyo, Japan) in diluted nitric or hydrochloric acid. These concentrations were titrimetrically standardized with EDTA. The commercial product of ammonia water (28%, Kanto Chemicals, Tokyo, Japan) was used as received. Sodium dodecylsulfate (SDS) (Wako Pure Chemicals, Tokyo, Japan) and sodium chloride (Kanto Chemicals, Tokyo, Japan) solutions were prepared by dissolving these reagents in water. All chemicals were of analytical grade and were dissolved in deionized water.

### 2.2. Apparatus

The absorbance measurement was performed using a Shimadzu UV-265 spectrophotometer with quartz cells of 1.0 cm

path length. The metal concentration was determined using a Shimadzu AA-625-11 flame atomic absorption spectrometer (AAS) or a Varian LIBERTY SERIES II inductively coupled plasma atomic emission spectrometer (ICP-AES). All the pH measurements were performed using a Horiba M-7 pH meter in combination with a glass electrode. A Hitachi Himac CF7D2 centrifuge was used for the phase separation.

### 2.3. Procedure

#### 2.3.1. Extraction of a metal ammine-complex into the SDS gel phase

A solution containing divalent metals was separately transferred to a 10 cm<sup>3</sup> centrifuge tube with a graduation line. After successively adding ammonia water and SDS aqueous solution, the solution was shaken to form the ion-pair. Sodium chloride solution was then added as a salting-out reagent and the mixture was diluted to a marked line with water. After cooling the solution in an ice-water bath and centrifuging (0 °C, 5000 rpm, 10 min), the aqueous and SDS phases were separated. The SDS phase located at the bottom was a gel-like solid.

#### 2.3.2. Recovery of a metal ion by back-extraction

In order to recover the metal ion from the gel phase, it is necessary to decompose the ion-pair. Hydrochloric acid was added to the SDS phase containing the metal ammine-complex after the removal of the aqueous phase. Sodium chloride solution was then added and diluted to a marked line with water. By cooling and centrifuging, the metal ion was recovered into the aqueous phase.

## 3. Results and discussion

### 3.1. Influence of metal concentration on the extraction of an ammine-complex

The optimal extraction conditions were between  $3.8 \times 10^{-2}$  and  $7.0 \text{ mol dm}^{-3}$  for ammonia,  $4.2 \times 10^{-3}$  and  $0.15 \text{ mol dm}^{-3}$  for SDS and  $6.8 \times 10^{-2}$  and  $0.62 \text{ mol dm}^{-3}$  for sodium chloride. The effect of the metal concentration on the extractability was investigated and is shown in Fig. 1. The different concentrations at which the ion-pair was extracted were observed for each metal. The order of extractability was palladium(II) > copper(II) > nickel(II) > zinc(II)  $\approx$  platinum(II).

### 3.2. Application and limit of general liquid–liquid extraction model to ionic surfactant system

As a rule, the phenomenon for ion-pair extraction has been explained by the liquid–liquid extraction model. For example, the distribution ratio,  $D$ , between the aqueous and gel phases

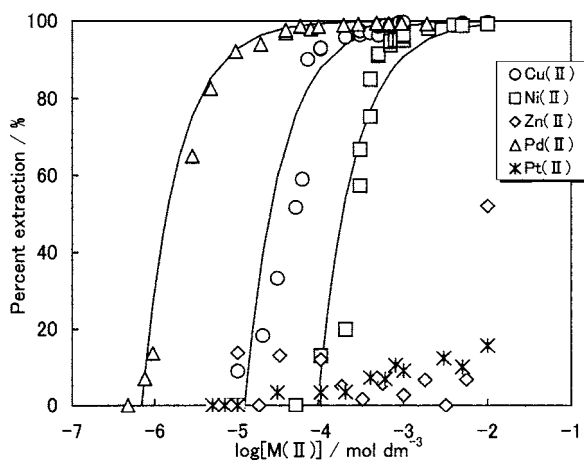


Fig. 1. Effect of metal concentration on the percent extraction of ion-pairs and theoretical curves based on their solubility product  $[\text{NH}_3] = 0.40 \text{ mol dm}^{-3}$ ,  $[\text{SDS}] = 6.24 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $[\text{NaCl}] = 0.27 \text{ mol dm}^{-3}$ .

is defined for the ion-pair of copper(II) ammine-DS

$$D = \frac{[\text{Cu}(\text{NH}_3)_4(\text{DS})_2]_{\text{gel}}}{[\text{Cu}(\text{NH}_3)_4^{2+}]_{\text{aq}} + [\text{Cu}(\text{NH}_3)_4(\text{DS})_2]_{\text{aq}}} \quad (1)$$

where the subscripts aq and gel denote the aqueous and gel phases, respectively. Assuming that the ion-pair concentration is negligibly small in the aqueous phase, Eq. (1) is rewritten as follows:

$$D = \frac{[\text{Cu}(\text{NH}_3)_4(\text{DS})_2]_{\text{gel}}}{[\text{Cu}(\text{NH}_3)_4^{2+}]_{\text{aq}}} \quad (2)$$

The extraction constant of ion-pair,  $K_{\text{ex}}$ , is

$$K_{\text{ex}} = \frac{[\text{Cu}(\text{NH}_3)_4(\text{DS})_2]_{\text{gel}}}{[\text{Cu}(\text{NH}_3)_4^{2+}]_{\text{aq}} [\text{DS}^-]_{\text{aq}}^2} \quad (3)$$

where  $[\text{DS}^-]_{\text{aq}}$  represents the concentration of the SDS anion in the aqueous phase after phase separation. This equation is substituted in Eq. (2), giving

$$\log D = 2 \log [\text{DS}^-]_{\text{aq}} + \log K_{\text{ex}} \quad (4)$$

The volumes of the two phases are a function of the surfactant concentrations. The relation of the distribution ratio and percent extraction,  $E$ , is

$$D = \frac{E}{100 - E} \frac{V_{\text{aq}}}{V_{\text{gel}}} \quad (5)$$

where  $V_{\text{aq}}$  and  $V_{\text{gel}}$  denote the volumes of the aqueous and gel phases, respectively.

The ratio of  $V_{\text{aq}}/V_{\text{gel}}$  was 10 at  $6.24 \times 10^{-2} \text{ mol dm}^{-3}$  of the SDS concentration. The obtained values of  $\log K_{\text{ex}}$  are given in Table 1. The metal group of zinc(II) and platinum(II) having the low extraction constants was easily separable from that of copper(II) nickel(II) and palladium(II). On the other hand, the mutual separation of metals was difficult for copper(II), nickel(II) and palladium(II) by dependence of ex-

Table 1

Ion-pair extraction constants and solubility products, and the theoretical metal concentration remaining in aqueous phase after extraction

Metal	$\log K_{\text{ex}}$ ( $\text{mol dm}^{-3}$ ) <sup>-2</sup>	$-\log K_{\text{sp}}$ ( $\text{mol dm}^{-3}$ ) <sup>3</sup>	$[\text{M}(\text{NH}_3)_n^{2+}]_{\text{aq}}$ ( $\text{mol dm}^{-3}$ )
Cu(II)	8.34	$11.8 \pm 0.8$	$(1.21 \pm 0.14) \times 10^{-5}$
Ni(II)	8.77	$10.9 \pm 0.4$	$(9.18 \pm 0.92) \times 10^{-5}$
Pd(II)	8.66	$13.0 \pm 0.8$	$(6.96 \pm 0.78) \times 10^{-7}$
Zn(II)	1.29	—	—
Pt(II)	1.41	—	—

$$[\text{DS}^-]_{\text{aq}} = (3.83 \pm 0.18) \times 10^{-4} \text{ mol dm}^{-3}.$$

tractability on the SDS concentrations, because there are no differences among the  $K_{\text{ex}}$  values. As shown in Fig. 1, the extractability significantly depended on the metal concentrations, however, the general theory of liquid–liquid extraction was insufficient to explain the dependence of metal concentration on the extractability.

### 3.3. Extractability of metals as a function of solubility of the ion-pair

We thought that the extractability of the metals was affected by the solubility of the ion-pair forming in the aqueous solution. In the presence of a small amount of SDS, solution turbidity was observed. The solubility product of an ion-pair,  $K_{\text{sp}}$  is defined as follows:

$$K_{\text{sp}} = [\text{M}(\text{NH}_3)_n^{2+}]_{\text{aq}} [\text{DS}^-]_{\text{aq}}^2 \quad (6)$$

where  $[\text{M}(\text{NH}_3)_n^{2+}]_{\text{aq}}$  and  $[\text{DS}^-]_{\text{aq}}$  denote the equilibrium concentrations of the metal ammine-complex and dodecyl-sulfate anion in the aqueous phase, respectively. Since  $K_{\text{sp}}$  is a constant, the concentration of a metal ammine-complex ( $[\text{M}(\text{NH}_3)_n^{2+}]_{\text{aq}}$ ) is decreased with the increasing  $\text{DS}^-$  concentrations. As shown in Fig. 2, the percent extraction of the ion-pairs of copper(II), nickel(II) and palladium(II) linearly increased with the increasing SDS concentration be-

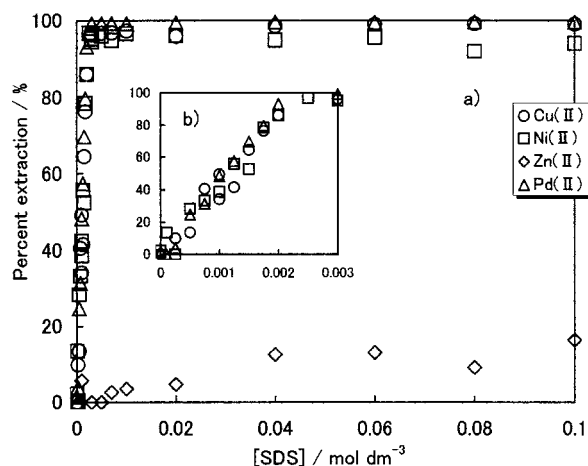


Fig. 2. Effect of SDS concentration on the percent extraction of ion-pairs  $[\text{M(II)}] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{NH}_3] = 0.40 \text{ mol dm}^{-3}$ ,  $[\text{NaCl}] = 0.27 \text{ mol dm}^{-3}$ .

tween 0 and  $0.0025 \text{ mol dm}^{-3}$ ; however, the zinc(II) ammine-complex was not extracted even at a  $0.10 \text{ mol dm}^{-3}$  SDS concentration.

The initial volume,  $V$ , of the solution is divided into that of the aqueous phase and gel phase after the phase separation.

$$V = V_{\text{aq}} + V_{\text{gel}} \quad (7)$$

The molar amount of SDS in the initial solution is

$$[\text{SDS}]_{\text{ini}} V = [\text{DS}^-]_{\text{aq}} V_{\text{aq}} + 2\{\text{M}(\text{NH}_3)_n(\text{DS})_2\}_{\text{solid}} + [\text{SDS}]_{\text{gel}} V_{\text{gel}} \quad (8)$$

where  $[\text{SDS}]_{\text{ini}}$  and  $\{\text{M}(\text{NH}_3)_n(\text{DS})_2\}_{\text{solid}}$  represent the SDS concentration in the initial solution and the molar amount of the ion-pair, respectively. The gel phase consists of water molecules and SDS;  $[\text{SDS}]_{\text{gel}}$  denotes the concentration of SDS in the gel phase. The  $[\text{DS}^-]_{\text{aq}}$  could not be calculated using Eq. (8) because the value of  $[\text{SDS}]_{\text{gel}}$  was unknown. Therefore, the  $[\text{DS}^-]_{\text{aq}}$  was measured by the ethylviolet absorptiometric method [23] ( $[\text{DS}^-]_{\text{aq}} = (3.83 \pm 0.18) \times 10^{-4} \text{ mol dm}^{-3}$ ). This value was much lower than the critical micelle concentration ( $\text{CMC} = 8.2 \times 10^{-3} \text{ mol dm}^{-3}$ ) reported in pure water at  $25^\circ\text{C}$  [24]. The CMC may be influenced by the presence of salts and temperature. When the  $[\text{DS}^-]_{\text{aq}}$  is lower than  $3.83 \times 10^{-4} \text{ mol dm}^{-3}$ , no gel phase was formed. In the absence of  $[\text{SDS}]_{\text{gel}} V_{\text{gel}}$ , Eq. (8) can be written as follows:

$$[\text{SDS}]_{\text{ini}} V = [\text{DS}^-]_{\text{aq}} V_{\text{aq}} + 2\{\text{M}(\text{NH}_3)_n(\text{DS})_2\}_{\text{solid}} \quad (9)$$

$$[\text{DS}^-]_{\text{aq}} = \frac{[\text{SDS}]_{\text{ini}} V - 2\{\text{M}(\text{NH}_3)_n(\text{DS})_2\}_{\text{solid}}}{V_{\text{aq}}} \quad (10)$$

Eq. (10) is substituted in Eq. (6),

$$K_{\text{sp}} = [\text{M}(\text{NH}_3)_n^{2+}]_{\text{aq}} \times \left( \frac{[\text{SDS}]_{\text{ini}} V - 2\{\text{M}(\text{NH}_3)_n(\text{DS})_2\}_{\text{solid}}}{V_{\text{aq}}} \right)^2 \quad (11)$$

The molar amount of the metal in the initial solution is

$$[\text{M}]_{\text{ini}} V = [\text{M}(\text{NH}_3)_n^{2+}]_{\text{aq}} V_{\text{aq}} + \{\text{M}(\text{NH}_3)_n(\text{DS})_2\}_{\text{solid}} \quad (12)$$

Since the  $[\text{M}(\text{NH}_3)_n^{2+}]_{\text{aq}}$  was a measurable value, the  $\{\text{M}(\text{NH}_3)_n(\text{DS})_2\}_{\text{solid}}$  was determined from  $[\text{M}]_{\text{ini}} V$ . The solubility product of the ion-pair was calculated from the plots in Fig. 2(b) using Eq. (11). The values of  $-\log K_{\text{sp}}$  are given in Table 1.

When an excess of SDS was added, the concentration of SDS in the aqueous phase ( $[\text{DS}^-]_{\text{aq}}$ ) was constant. SDS in excess, at a concentration of more than  $3.83 \times 10^{-4} \text{ mol dm}^{-3}$ , deposited and formed the gel phase. Therefore, Eq. (11) could be rewritten as follows:

$$K_{\text{sp}} = \alpha [\text{M}(\text{NH}_3)_n^{2+}]_{\text{aq}} \quad (13)$$

$$\alpha = (3.83 \times 10^{-4} \text{ mol dm}^{-3})^2$$

Table 2

Mutual separation of copper(II) and nickel(II) in a real sample(nickel–copper alloy)

Metal	Extraction	
	Aqueous phase (%)	SDS phase (%)
Cu(II)	$86.8 \pm 5.1$	$7.3 \pm 2.4$
Ni(II)	$8.1 \pm 1.3$	$89.9 \pm 6.8$

Average  $\pm$  S.D. (six samples).

The value of  $[\text{M}(\text{NH}_3)_n^{2+}]_{\text{aq}}$ , calculated from Eq. (13), is the metal concentration at which the ion-pair began to be extracted and is given in Table 1 as  $[\text{M}(\text{NH}_3)_n^{2+}]_{\text{aq}}$ . From Eq. (13), it was found that the solubility product of an ion-pair was dependent on the metal concentration, thus, the metal concentration which remains in the aqueous phase can be calculated.

The equation related to the percent extraction and solubility product is:

$$E = \left( 1 - \frac{[\text{M}(\text{NH}_3)_n^{2+}]_{\text{aq}}}{[\text{M}]_{\text{ini}}} \right) \times 100 \quad (14)$$

$$E = \left( 1 - \frac{K_{\text{sp}}}{\alpha [\text{M}]_{\text{ini}}} \right) \times 100 \quad (15)$$

The extraction curves calculated using Eq. (15) are shown as the solid line in Fig. 1 for copper(II), nickel(II) and palladium(II). These results show that these experimental values are in good agreement with the theoretical curve, and that the extractability of the metals was given as a function of the solubility products.

### 3.4. The separation of metals

In order to estimate the capacity of the mutual separation of metals, a separation factor, SF, is defined as follows:

$$\text{SF} = \frac{[\text{M}_1]}{[\text{M}_2]} \quad (16)$$

where  $[\text{M}_1]$  and  $[\text{M}_2]$  are the first and second metal concentrations at 50% of extraction, respectively. These values were 5600 for  $[\text{Zn(II)}]/[\text{Pd(II)}]$ , 210 for  $[\text{Zn(II)}]/[\text{Cu(II)}]$ , 150 for  $[\text{Ni(II)}]/[\text{Pd(II)}]$ , 38 for  $[\text{Zn(II)}]/[\text{Ni(II)}]$ , 26 for  $[\text{Cu(II)}]/[\text{Pd(II)}]$  and 6 for  $[\text{Ni(II)}]/[\text{Cu(II)}]$ . Based on these numbers (SF), the mutual separations were examined for Ni(II)/Cu(II) and Pd(II)/Pt(II). The sample solution, which was prepared from a nickel–copper alloy, was  $2.0 \times 10^{-4} \text{ mol dm}^{-3}$  in nickel(II) and  $9.3 \times 10^{-5} \text{ mol dm}^{-3}$  in copper(II); the result of the separation is given in Table 2. Since the value of the separation factor,  $[\text{Ni(II)}]/[\text{Cu(II)}]$ , was small, a complete mutual separation was difficult.

The separation of palladium(II) and platinum(II) was performed. Although there are several methods for the separation of palladium(II) and platinum(IV) [25–28], the separation of palladium(II) and platinum(II) has been difficult. A mixed solution of  $1.0 \times 10^{-4} \text{ mol dm}^{-3}$  of

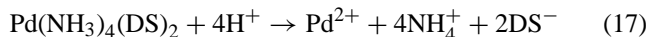
Table 3  
Mutual separation of palladium(II) and platinum(II)

Metal	Extraction (%)	Recovery (%)	Reference
Pd(II)	96.2 ± 0.7	93.2 ± 5.9	
Pt(II)	9.8 ± 1.2	10.1 ± 0.4	
Cu(II)	98.8 ± 0.2 <sup>a</sup>	98.8 ± 0.5 <sup>a</sup>	[18]
Zn(II)	2.3 ± 0.7 <sup>a</sup>	2.3 ± 0.7 <sup>a</sup>	[18]

Average ± S.D. (three samples).

<sup>a</sup> Double extraction or recovery.

palladium(II) and  $1.0 \times 10^{-4} \text{ mol dm}^{-3}$  of platinum(II) was transferred to a  $10 \text{ cm}^3$  centrifuge tube with a graduation line. A  $0.40 \text{ mol dm}^{-3}$  aliquot of ammonia water and  $6.24 \times 10^{-2} \text{ mol dm}^{-3}$  of SDS aqueous solution were then added. After mixing the solution,  $0.27 \text{ mol dm}^{-3}$  of sodium chloride solution was added and diluted to a marked line with water. By cooling and centrifuging, the aqueous phase and SDS phase were separated. Palladium(II) formed a palladium(II)-amine-DS ion-pair, and was incorporated into the SDS phase by the extraction procedure. On the other hand, platinum(II) remained in the aqueous phase and did not form an ion-pair. The extracted ion-pair of the palladium(II) ammine-complex with  $\text{DS}^-$  was decomposed by the addition of  $0.50 \text{ mol dm}^{-3}$  of hydrochloric acid, and was back-extracted as the palladium(II) ion into the aqueous phase. The formed ion-pair decomposes under acidic conditions; the equation is expressed as follows:



From the results in Table 3, palladium(II) and platinum(II) could be separated using this method. For reference, the result from a double extraction and recovery procedure for the mutual separation of copper(II) and zinc(II) in a brass alloy is also given in Table 3 [18]. As seen from the separation result for copper(II) and zinc(II) in Table 3, the separation efficiency is improved by repeating the extraction and back-extraction procedure.

### 3.5. Adsorption of the cationic ammine-complex on the anionic SDS gel

Since  $\text{DS}^-$  acts as a pairing-ion of an ammine-complex, we thought that the SDS gel could be used as an ion-exchanger. By cooling the solution of SDS below its Krafft point temperature, the SDS gel was prepared as follows: a solution containing ammonia, SDS and sodium chloride was transferred to a  $10 \text{ cm}^3$  centrifuge tube. The solution was then cooled and a gel-like solid of SDS was obtained. This SDS gel corresponded to the sodium salt of a cation exchange resin. The adsorption of copper(II), nickel(II) and palladium(II) ions was investigated at  $7^\circ\text{C}$  by a batch method. The results are expressed by the closed symbols in Fig. 3 with the experimental values expressed by the opened symbols of extraction method 2.3.1 for comparison. There are no significant differences between

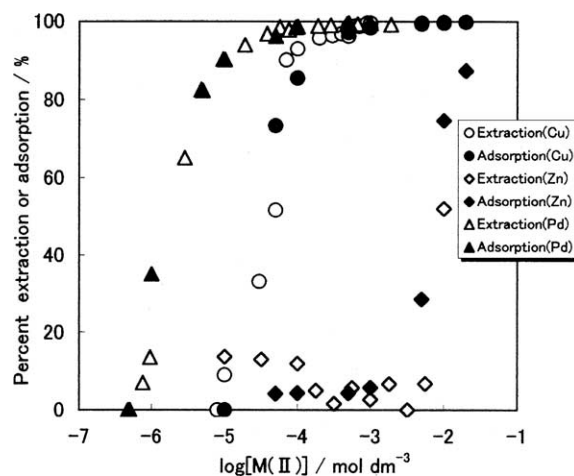


Fig. 3. Comparison with extraction and adsorption behavior  $[\text{NH}_3] = 0.40 \text{ mol dm}^{-3}$ ,  $[\text{SDS}] = 6.24 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $[\text{NaCl}] = 0.27 \text{ mol dm}^{-3}$ .

the extraction and adsorption behavior for all the metals tested.

The saturated adsorption of two ammine-complexes was determined. The initial concentration of SDS was  $1.0 \times 10^{-2} \text{ mol dm}^{-3}$ . Assuming an ion-pair of 1:2, and since the molecular weight of SDS is  $288 \text{ g mol}^{-1}$ , the amount of the saturated adsorption of an ammine-complex per 1 g of SDS is 1.73 mmol, which is expressed by the dotted line in Fig. 4. If the metal concentrations are increased, the extraction or adsorption of the metals did not overcome the saturation of the SDS gel within the experimental error. The electrostatic interaction between the cation and anion was an important factor as a driving force for the extraction and adsorption of the metals. A better separation efficiency will be expected by applying this extraction method to a column method.

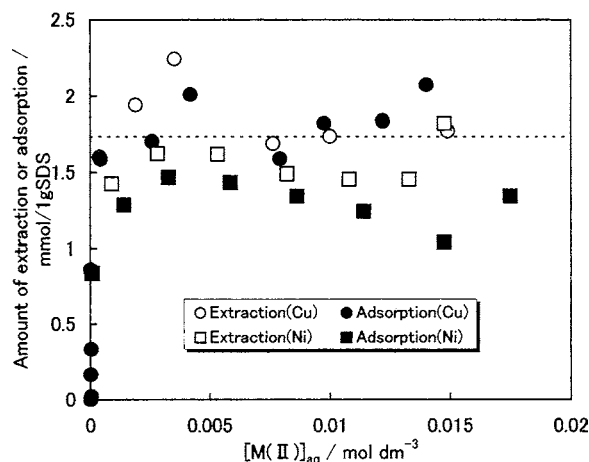


Fig. 4. Comparison with the saturated amount of extraction and adsorption  $[\text{NH}_3] = 0.40 \text{ mol dm}^{-3}$ ,  $[\text{SDS}] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $[\text{NaCl}] = 0.27 \text{ mol dm}^{-3}$ .



#### 4. Conclusion

The anionic surfactants, such as SDS, play two roles as the extraction medium and the pairing-ion for the cationic complexes. The ammine-complexes of metals formed ion-pairs with SDS and were extracted into the surfactant phase. The metal extractability was examined using a general liquid–liquid extraction model. After the phase separation, the concentration of the SDS monomer was constant and low in the aqueous phase. The 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. The complex of copper(II), nickel(II) and palladium(II) form the ion-pair with the dodecylsulfate anion ( $\text{DS}^-$ ) and were extracted into the SDS gel phase, on the other hand, the metals such as zinc(II) and platinum(II) did not form an ion-pair and remained in the aqueous phase. This was applied to the mutual separation of the metals of Ni(II)/Cu(II) and Pd(II)/Pt(II). The extraction accompanying the ion-pair formation is characteristic of ionic surfactant systems and will be used to the pre-concentration and mutual separation of metals for practical use.

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