An X-ray Study of the Surfactant Gel Extraction Method Separation Mechanism and Its Application to Separate Nickel(II) from Copper(II) and as Ammine-Complexes Using the Anionic Surfactant SDS

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A micellar solution of sodium dodecylsulfate (SDS) can separate into two phases due to a temperature change or the addition of salts. SDS plays the roles of a pairing-ion for ammine-complexes and of an extraction medium. The ion-pair extraction mechanism was investigated by SAXS and DSC measurements. This extraction was used for the separation of Cu(II) as a minor component from Ni(II) as a dominant component.

1. Introduction

Interest has been shown in the separation of metal ions by extraction and/or adsorption methods which use a surfactant and a polymer electrolyte of a solid or a liquid as the extraction medium.¹⁻⁵ A micellar solution of an ionic surfactant can separate into two phases due to a temperature change or the addition of salts. One is a surfactant-depleted phase (aqueous phase) and the other is a surfactant-rich phase (surfactant phase). Based on this phase separation phenomenon, surfactant extraction techniques⁶⁻¹¹ have great potential in industrial applications for removal of organic pollutants and recovery of heavy metals from waste water.

An anionic surfactant, SDS, which has low toxicity and is easily biodegraded, has been used for many kinds of metal extraction as the extraction medium. In our work, we also employed ammonia as the complexing agent for metal ions. Ammonia is an important and inexpensive industrial substance and has a large number of uses. Nickel(II), Cu(II) and Zn(II) ion formed ammine complexes in ammonia medium

and are extracted into the SDS gel after ion-pair formation with the dodecylsulfate anion (DS⁻).¹¹ In the extraction of ammine complexes, the extractability of metals reduced with lower metal concentration. This phenomenon did not occur in traditional extraction systems and was explained by the solubilisation of these ion-pairs with DS⁻ and M(NH₃)₄²⁺, where M is a metal ion. In the SDS solution, which involves a solid SDS gel, the concentration of the monomer DS⁻ in the aqueous phase is constant and the percent extraction(*E*%) is described using the ion-pair solubility product

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

where α is the concentration of the SDS monomer in the aqueous phase, and K_{sp} is the solubility constant of the ion-pairs.¹¹ We also confirmed that thiourea - complexes formed ion-pairs with the anionic surfactant,¹² and that the chloro complexes also formed ion-pairs with the cationic surfactant.¹³⁻¹⁵

The purpose of the present study was to clarify the properties of the ion-pairs and to propose a new separation method for metal ions. We verified the formation of specific ion-pair crystals using X-ray diffraction and differential scanning calorimetry. Our hypothesis to explain the extraction mechanism was based on the formation of a new surfactant gel phase composed of metal ions and DS⁻.

2. Experimental

2.1 Reagents and chemicals

The 1.00×10^{-2} mol dm⁻³ stock solutions of Cu(II), Ni(II) and Pd(II) were separately prepared by dissolving weighed amounts of copper(II) nitrate trihydrate (Kishida Chemicals, Tokyo) and nickel(II) nitrate hexahydrate (Wako Pure Chemicals, Tokyo) in 100 cm³ of 0.1 mol dm⁻³ nitric acid, or palladium(II) chloride (Kanto Chemicals, Tokyo) in 100 cm³ of 0.1 mol dm⁻³ hydrochloric acid. The anionic surfactant, 20%(w/v) dodecyl sulfate, (SDS, Wako Pure Chemicals, Tokyo), was prepared by dissolving the reagent in deionized water without further purification. The salting-out reagent, 20%(w/v) sodium chloride, (Kanto Chemicals, Tokyo), was prepared by dissolving it 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) or a Shimadzu AA-625-11 atomic absorption spectrophotometer. A Hitachi Himac CF7D2 centrifuge was used for phase separation. Small angle X-ray measurements (SAXS) were performed using a Brucker AXS DIP-220 powder X-ray diffractometer using copper K α radiation. Polarized light microscope images were obtained using a Nikon ECLIPSE E600.

2.3 Procedure

Isolation of the metal-surfactant ion-pair for SAX analysis

A solution containing 180 or 90 μ mol of Cu(II), Ni(II) or Pd(II) was transferred to a 10 cm³ centrifuge tube with a graduation line. After successively adding 0.27cm³ of 28 % ammonia and 0.5 cm³ of

a 20% (w/v) SDS (360 μmol) solution, the final solution was shaken to form the ion-pair. Sodium chloride solution (0.25 cm^3) was then added and the mixture was diluted to the mark with deionized water. After cooling the solution in an ice-water bath and centrifuging (5000 rpm, 10 min, $0\text{ }^\circ\text{C}$), the aqueous and SDS phases were separated. The aqueous phase was discarded, the SDS phase was subjected to gel structure measurement by small angle XRD (SAXS) or differential scanning calorimetry (DSC), respectively.

Separation of nickel(II) from copper(II)

A solution containing 2 μmol of Cu(II) and 0.04 μmol of Ni(II) was transferred to a 10 cm^3 centrifuge tube with a graduation line. After successively adding 0.27 cm^3 of ammonia and 0.5 cm^3 of a 20% (w/v) SDS solution, the solution was shaken to form the ion-pair. The 0.25 cm^3 sodium chloride solution was then added and the mixture was diluted to the mark with deionized water. After cooling the solution in an ice-water bath and centrifuging (5000 rpm, 10 min, $0\text{ }^\circ\text{C}$), the aqueous and SDS phases were separated. The aqueous phase was transferred to another tube and its metal concentration determined by ICP-AES in order to calculate the percent extraction of the metal ions.

3. Results and Discussion

SDS deposits as a gel-like solid from aqueous solution on adding a salting out reagent or cooling. Ammine complexes of Co(II), Ni(II) and Pd(II) are extracted into the SDS gel.¹¹ We identified the phenomenon in which the extractability of Pd(II), Ni(II) and Cu(II) complexes into the SDS phase decreased at low metal concentrations, and the dependences of the metal concentrations on $E(\%)$ were explicable by K_{sp} , respectively. To explain the mechanism of formation of these ion-pairs, the properties of the ion-pairs requires elucidation.

3.1 Polarized light microscope image

Figure 1 is a polarized light microscope image of the separated SDS phase containing ion pair of Cu(II) complex with DS^- at room temperature (about $25\text{ }^\circ\text{C}$). A part of the SDS phase melted at this temperature and the polarized light disappeared. The liquefied part is the dark portion surrounded by white lines. The crystals of the $[\text{Cu}(\text{NH}_3)_4(\text{DS})_2]$ ion-pairs did not liquefy and were identified by polarized light.

Fig. 1 Polarized light microscope image of the SDS phase.

3.2 Melting point measurement

The melting point of the SDS gel containing Cu(II) ion, separated from the water phase by the addition of NaCl, was measured by DSC. As shown in Fig. 2, three endothermic peaks were observed at $0\text{ }^\circ\text{C}$, $20\text{ }^\circ\text{C}$, and $77\text{ }^\circ\text{C}$ representing ice melting,

the SDS gel melting, and the $[\text{Cu}(\text{NH}_3)_4(\text{DS})_2]$ ion-pair melting, respectively. These results suggest independent formation of the pure SDS and metal ion-pair gels.

3.3 SAXS analysis

The formation of the ion-pair in the SDS phase was verified using SAXS measurements. As the obtained SDS phase was a liquid at room temperature, therefore, the SAXS sample cell was cooled using liquid nitrogen vapor. It is already known that the SDS have lamellar structures.^{16,17} The SAXS pattern for the pure SDS phase, which contained SDS and water but no metal-ammine complex, also possessed one reflection peak at 3.06° ($d_{001} = 2.88$ nm, Fig.3a) exhibiting a lamellar structure. On the other hand, the SDS phase with a composition of $1 : 2 = \text{Cu(II)} : \text{SDS}$ showed a reflection peak at 3.56° ($d_{001} = 2.48$ nm, Fig.3c). At a mole ratio of $1 : 2$, all the SDS completely reacted with the Cu(II) ammine complex. This ion-pair, $[\text{Cu}(\text{NH}_3)_4(\text{DS})_2]$, also showed a lamellar structure. There are two possible mechanisms for the formation of the ion-pair of the Cu(II) complex with DS^- . One is the intercalation of $[\text{Cu}(\text{NH}_3)_4]^{2+}$ by ion-exchange with Na^+ in the hydrophilic layer of the SDS gel and SAXS will show only one reflection peak which shifts from low to high angles (2θ) depending on the Cu(II) concentration. The other is the independent formation in which two reflection peaks corresponding to pure SDS and the ion-pair $[\text{Cu}(\text{NH}_3)_4(\text{DS})_2]$ will appear in the SAXS pattern. The phase in which the molar ratio was $1 : 4 = \text{Cu(II)} : \text{SDS}$ gave two peaks at 3.06° ($d_{001} = 2.88$ nm) and 3.54° ($d_{001} = 2.49$ nm) corresponding to the pure SDS and the Cu(II) ion-pair (Fig.3b). The same results were obtained for Ni(II) and Pd(II) with basal spacings of $d_{001} = 2.02$ and 2.95 nm, respectively.

In Fig.4, the SAXS pattern of the SDS phase obtained from an aqueous solution containing 1×10^{-4} mol dm^{-3} of Cu(II)- and 1×10^{-4} mol dm^{-3} Ni(II)- ammine complexes and excess SDS is shown together with those of pure SDS, $[\text{Cu}(\text{NH}_3)_4(\text{DS})_2]$, and $[\text{Ni}(\text{NH}_3)_4(\text{DS})_2]$. As shown in Fig.4, peaks at 3.06° , 3.56° , and 4.38° appeared corresponding to pure SDS, $[\text{Cu}(\text{NH}_3)_4(\text{DS})_2]$ and $[\text{Ni}(\text{NH}_3)_4(\text{DS})_2]$, respectively, at

Fig. 2 The DSC curve for the SDS phase.

Fig. 3 SAXS patterns for (a) pure SDS, (b) SDS + Cu(II) ion-pair, (c) Cu(II) ion-pair.

their original positions. It is concluded that the SDS phase consisted of pure Cu(II) ion-pair, Ni(II) ion-pair and pure SDS gel as shown in Fig.5. It is clear that these ion-pairs formed independently.

3.4 Separation of Cu(II)-Ni(II) mixture

The separation of Cu(II) and Ni(II) was attempted using the present method of surfactant gel precipitation-extraction (SGE). If the SGE method can prevent the co-precipitation of existing metal ions, the major component will be removed from the minor component when the concentration is less than its solubility. The SGE method was carried out for a sample of Cu(II) : Ni(II) = 50 : 1. As described in a previous paper,¹¹ the nickel(II)-ammine complex was not extracted at a concentration of $4.0 \times 10^{-6} \text{ mol dm}^{-3}$, whereas the copper(II)-ammine complex was extracted at a concentration of $2.0 \times 10^{-4} \text{ mol dm}^{-3}$. Nickel(II) was not extracted from the mixed solution of copper(II) and nickel(II) ions of each concentration as reported above under these conditions, therefore, co-precipitation or occlusion of nickel(II) ions was not observed. The percent extractions obtained for Cu and Ni were $98.3 \pm 0.7 \%$ and $-0.7 \pm 1.1 \%$ respectively based on three measurements.

Most of the conventional precipitation methods are accompanied by the co-precipitation of many metal ions and therefore lack selectivity. The present SGE method could separate the minor and major components and is regarded as a new separation method.

Fig.4 SAXS patterns for (a) SDS + Cu(II) ion-pair + Ni(II) ion-pair, (b) SDS, (c) Cu(II) ion-pair, (d) Ni(II) ion-pair.

Fig.5 The schematic lamellar structures of the SDS phase consisting of Cu(II) ion-pairs and pure SDS gel.

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