Notes

Stripping of Cadmium(II) Xanthato Complexes from the Anionic Surfactant Phase of Sodium Dodecylsulfate Gel to the Aqueous Phase

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Traditionally, organic solvents, such as benzene or chloroform, have been used for liquid-liquid extraction systems; however, these solvents are often carcinogenic, toxic and cause environmental pollution. Surfactants have a non-volatile nature and are relatively harmless reagents. An aqueous solution containing surfactants exhibits the property of being separated into two phases due to a temperature change or the addition of salts. Based on these phase-separation phenomena, the surfactant-extraction technique was investigated with interest for chemical analyses involving the separation and quantitative determination of a large number of metal ions.¹⁻⁴ To our knowledge, however, there have been no investigations concerning the recovery of the metal ions from the extracts of the surfactant. This process corresponds to the so-called back- or reverse-extractions in the conventional liquid-liquid extraction system. We prepared a series of xanthates (*O*-alkyldithiocarbonate, ROC(S)S^- , abbreviated as X^-) as ligands and investigated the extraction and the stripping of Cd(II) in the forms of xanthato complexes between the two phases of an anionic surfactant of sodium dodecylsulfate (SDS) gel and water.

Experimental

Reagents

A 0.05 mol dm⁻³ stock solution of Cd(II) was prepared by dissolving a weighed amount of cadmium chloride (Kanto Chemicals) in 0.1 mol dm⁻³ hydrochloric acid, then titrimetrically standardized with EDTA. We prepared 20%(w/v) SDS (Merck) and 25%(w/v) sodium chloride solutions by dissolving weighed amounts in water, respectively. The potassium salts of ethyl- (EtX), butyl- (BuX), and hexylxanthate (HeX), and the sodium salts of octyl- (OcX), decyl- (DeX), dodecyl- (DoX) and tetradecylxanthate (TeX) were prepared using a previously reported method.⁵ These reagents were recrystallized three times from acetone and 1.0×10⁻² mol dm⁻³ aqueous solutions were prepared. A 500 cm³ buffer solution was prepared by dissolving 30.3 g of tris(hydroxymethyl)aminomethane (Wako Pure Chemicals) in water and

adjusting the pH to 8.0 with hydrochloric acid. All other chemicals were of analytical grade.

Apparatus

AAS measurements were made using a Shimadzu AA-625-11 flame atomic absorption spectrometer. All pH measurements were made with a Horiba M-7 pH meter and a combination glass electrode.

General procedure

A solution containing Cd(II) was transferred to a 10 cm³ centrifuging tube with a graduation line. After the successive addition of 1.0 cm³ of buffer, 1.25 cm³ of SDS and 1.0 cm³ of xanthate solutions, the solution was diluted to 6.0 cm³ with water. After shaking the solution, 4.0 cm³ of a NaCl solution was added. After centrifugation, the upper aqueous phase was discarded. The SDS phase that remained at the bottom of the tube was diluted to 10 cm³ with water. After phase separation by cooling, the concentration of Cd(II) in the aqueous phase was measured by AAS.

Results and Discussion

Phase separation

An SDS gel phase was generated by the addition of an electrolyte, such as NaCl, or cooling the solution to under its Krafft point temperature. The water content in the gel phase, which was estimated from the reduced weights by drying under a vacuum at 60°C, was about 80% when the phase separation was maintained by a method based on the salting out effect. It was about 90% by a separation method based on the cooling effect. The volume of the gel phase depended on the concentration of SDS, and was about 1.0 cm³ for a 2.5% SDS solution.

Extraction of xanthate

Most of the xanthates in the solution were deprotonated at pH=8, and resulted in anionic species of X^- . Figure 1 shows the effect of the alkyl chain length of X^- on the extraction of the xanthates. While small ligands of EtX, BuX and HeX were hardly extracted into the SDS phase by salting out, the large and hydrophobic xanthates were increasingly extracted. On the other

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Fig. 1 Effect of the alkyl-chain length on the percent extraction of xanthate. [SDS]=2.5%(w/v), [X]= 2.0×10^{-3} mol dm $^{-3}$, pH=8. ○: separation by the addition of 10%(w/v) NaCl. ●: separation by cooling.

hand, all xanthates were not extracted by separation based on the cooling effect. Therefore, TdX and DoX were almost stripped into the aqueous phase, and a part of DeX and OcX after the separation by cooling.

Extraction of complexes

Cd(II) formed xanthato complexes that were sparingly soluble in both water and SDS micelle. When the micelle was destroyed by the addition of an electrolyte, the complexes were transferred into the SDS phase. The optimal condition of extraction for the Cd(II) complex with DoX was almost the same as that for those with other xanthates, as follows: the concentrations of SDS and NaCl were 1–4% and 8–12%, respectively. As shown in Fig. 2, a stable and constant absorbance was obtained at a pH higher than 7, while the DoX was decomposed and absorbance was reduced with time at a pH lower than this value.

Figure 3 shows the recovery of Cd(II) as a function of the concentration of xanthates, where the recovery was calculated by the Cd(II) quantities measured before and after the stripping. All xanthato complexes were extracted into the SDS phase by salting out. On the other hand, Cd(II) was completely stripped using TeX, DoX and DeX, and was partially stripped using OcX after phase separation by cooling. None or a small amount of Cd(II) was stripped with EtX, BuX and HeX into the aqueous phase.

Below the Krafft point temperature, there are no SDS micelles in the aqueous phase, because the solution includes a few surfactants. We previously reported that large xanthates, such as DoX, acted as not only the ligand for metals, but also as surface-active agents.⁵ Large xanthato complexes with Cd(II), which were stripped from the SDS gel phase, were dissolved by the micelle of xanthates or dispersed as microemulsion in the aqueous phase after separation by cooling. However, the complexes of EtX, BuX and HeX remained in the surfactant phase after phase separation by cooling, because these complexes are insoluble in water. The stripping of

Fig. 2 Effect of the pH on the percent extraction of Cd(II). [Cd(II)]= 5.0×10^{-5} mol dm $^{-3}$. [SDS]=2.5%(w/v). ○: with 2.0×10^{-3} mol dm $^{-3}$ DoX. ●: without xanthate.

Fig. 3 Effect of the concentration of xanthate on the percent extraction of Cd(II). X=(Δ) TeX, (□) DoX, (○) DeX, (▽) OcX, (■) HeX, (▲) BuX and (●) EtX. [Cd(II)]= 5.0×10^{-5} mol dm $^{-3}$. [SDS]=2.5%(w/v). [NaCl]=10%(w/v), pH=8.

Cd(II) was performed with a 2.5×10^{-2} mol dm $^{-3}$ EDTA solution after extraction of Cd(II) as the EtX complex. More than 96% of Cd(II) was recovered. The extraction species seemed to change from CdX₂ to the water-soluble [Cd(EDTA)]²⁻ by the addition of EDTA.

The proposed extraction method can be widely applicable to recover metals in seawater and high-salinity wastewater; it will also be possible to recycle surfactants.

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