NOTES

SOLVENT EXTRACTION OF MOLYBDENUM(V) WITH ETHYL-XANTHATE OR DIPHENYLCARBAZONE

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Solvent extraction of molybdenum(V) with ethylxanthate and diphenylcarbazone (HDPCO) was investigated. When the perchloric acid concentration was above 0.2 mol dm^{-3} , a $1.32 \times 10^{-4} \text{ mol dm}^{-3}$ molybdenum(V) was completely extracted with $1.39 \times 10^{-2} \text{ mol dm}^{-3}$ ethylxanthate into chloroform. The extracted species contained molybdenum and ethylxanthate in a 1 : 2 molar ratio. Solid dark green complex formulated as $\text{Mo}_2\text{O}_3(\text{C}_2\text{H}_5\text{OCS}_2)_4$ was prepared. One molybdenum-oxygen-molybdenum bond in $\text{Mo}_2\text{O}_4^{2+}$ was suggested to be cleaved on the coordination of ethylxanthate. The optimum pH for the extraction of molybdenum(V) with HDPCO was 2.2, 2.7 and 3.8 for chloroform, nitrobenzene and n-butylacetate, respectively. The complex extracted was formulated as $\text{Mo}_2\text{O}_3(\text{DPCO})_4$. Two molybdenum (V) atoms are bridged with one oxo group.

Solvent extraction of molybdenum(VI) has been extensively studied because of its importance in biological and industrial chemistry. The study of the extraction of molybdenum(V) ¹⁾²⁾, however, is relatively few compared with those of molybdenum(VI) ³⁾.

Alkylxanthate has been of interest in the solvent extraction of metal ions because this reacts with various metal ions to provide solvent extractable complexes. Many devised methods for the solvent extraction-spectrophotometric determination of molybdenum(VI) with ethylxanthate have been described ⁴⁾. Blake et al. described that two molybdenum(V) atoms in $\text{Mo}_2\text{O}_3(\text{C}_2\text{H}_5\text{OCS}_2)_4$, which was prepared with the reaction of molybdenum(VI) with ethylxanthate, were bridged with one oxo group ⁵⁾.

In a preceding work, molybdenum(V) was found to be extracted with dithizone (H_2Dz) into chloroform and benzene as $\text{Mo}_2\text{O}_4(\text{HDz})_2(\text{H}_2\text{O})_2^{2)}$.

In this work, we studied the extraction behavior of molybdenum(V) with hard diphenylcarbazone having a similar molecular structure to dithizone and with ethylxanthate as a typical soft ligand.

EXPERIMENTAL

Reagent

Potassium ethylxanthate (Kanto Co. Ltd.) was purified from ethanol-water mixture. Diphenylcarbazone (Kanto Co. Ltd.) was purified by the method described in the reference ⁶⁾. Working solutions of HDPCO were prepared by dissolving a given amount of HDPCO into organic solvent just before the use. Molybdenum(V) perchlorate, $\text{Mo}_2\text{O}_4(\text{ClO}_4)_2$ was prepared and analysed as reported in the reference ²⁾. Working

solution of molybdenum(V) was prepared by diluting a stock solution with redistilled water before the use. The organic solvents were distilled before the use.

All the other reagents were of analytical grade.

Apparatus

The pH measurements were conducted by using a Hitachi-Horiba M-7 type pH meter. A Hitachi 170-30 type atomic absorption spectrophotometer was used for the determination of molybdenum(V). A Hitachi EPS-3 type spectrophotometer was employed to measure the absorption spectra of molybdenum(V)-DPCO and molybdenum(V)-ethylxanthate.

Procedures for the extraction

Ten cm^3 of $1.32 \times 10^{-4} \text{ mol dm}^{-3}$ molybdenum(V) solution, 10 cm^3 of a given concentration of ethylxanthate solution and 20 cm^3 of chloroform were pipetted into a 100 cm^3 -separatory funnel. The shaking for 3 min provided the constant extraction. Therefore, the solution was shaken for 5 min. Two phases were separated as rapidly as possible because of unstableness of the extracted molybdenum(V)-ethylxanthate in chloroform. After the separation of two phases, molybdenum in an aqueous phase was determined. Almost the similar procedure was used for the extraction of molybdenum(V) with diphenylcarbazone.

Preparation of $\text{Mo}_2\text{O}_3(\text{C}_2\text{H}_5\text{OCS}_2)_4$

Fifty cm^3 portion of $3.62 \times 10^{-2} \text{ mol dm}^{-3}$ molybdenum(V) in $2.0 \text{ mol dm}^{-3} \text{ HClO}_4$ was added to a 50 cm^3 portion of $3.00 \times 10^{-1} \text{ mol dm}^{-3}$ potassium ethylxanthate aqueous solution at $0 - 5^\circ\text{C}$. After allowing the solution to be stirred for 10 min, molybdenum(V)-ethylxanthate was extracted into a 30 cm^3 portion of chloroform. The extract was washed with a 50 cm^3 portion of redistilled water. Chloroform was evaporated quickly. A tarry product was obtained. The dark green crystal (yield 0.5 g) was formed on crystallization from benzene - heptane. Anal. Calcd for $\text{Mo}_2\text{O}_3(\text{C}_2\text{H}_5\text{OCS}_2)_4$: H, 2.78%; C, 19.89%. Found: H, 2.83%; C, 20.49%.

RESULTS AND DISCUSSION

Extraction of molybdenum(V) with ethylxanthate

Figure 1 represents the pH-dependency of the extraction of molybdenum(V) with ethylxanthate into chloroform, where the pH value was adjusted by using perchloric acid solution. Thus, $1.32 \times 10^{-4} \text{ mol dm}^{-3}$ molybdenum(V) was completely extracted with $1.39 \times 10^{-2} \text{ mol dm}^{-3}$ ethylxanthate into chloroform below pH 1.5. In the pH range 1.0 to about 4.0, the extraction percentage increases on both sides of pH 2.2.

Fig. 1 Effect of pH on the extraction of molybdenum(V) with ethylxanthate into chloroform.

Molybdenum(V): $1.32 \times 10^{-4} \text{ mol dm}^{-3}$; Ethylxanthate: $1.39 \times 10^{-2} \text{ mol dm}^{-3}$. The pH value was adjusted by using perchloric acid solution.

This pH effect can not be explained. Above pH 4.0, the extraction percentage decreases with increasing the pH value. This may be ascribed to the hydrolysis and polymerization of molybdenum(V).

The plots of $\log D$ vs. $\log$ [ethylxanthate] at pH 2.0 provided the straight line with a slope of 2.0, suggesting that the molar ratio of molybdenum(V) (as monomer) : ethylxanthate in the extracted molybdenum(V)-ethylxanthate is 1 : 2.

The ^1H NMR spectrum of the isolated molybdenum(V)-ethylxanthate in CDCl_3 shows the typical signals due to the methyl (3H, δ = 1.47 ppm from TMS, t, J = 7.2 Hz) and methylene (2H, δ = 4.61 ppm, q, J = 7.2 Hz) group of ethylxanthate, respectively. The signals due to water molecule were not detected.

The infrared spectrum of the isolated molybdenum(V)-ethylxanthate was quite similar to that of $\text{Mo}_2\text{O}_3(\text{C}_2\text{H}_5\text{OCS}_2)_4$ ⁷⁾ prepared from the reaction of Na_2MoO_4 or $(\text{NH}_4)_2\text{MoOCl}_5$ with ethylxanthate. The strong band at 431 cm^{-1} was assigned to a molybdenum-oxygen-molybdenum stretching mode⁷⁾. In addition, the electronic absorption spectrum of the extracted ethylxanthate in chloroform was also quite similar to that of the isolated ethylxanthate.

Based on these results and facts, the ethylxanthate complex extracted at pH 2.0 is formulated as $\text{Mo}_2\text{O}_3(\text{C}_2\text{H}_5\text{OCS}_2)_4$. The complex extracted above pH 2.2 may have different composition and structure.

Extraction of molybdenum(V) with HDPCO

The absorption spectra of molybdenum(V)-DPCO complex extracted into chloroform, n-butylacetate and nitrobenzene were shown in Fig. 2. The spectra in these organic solvents were not largely different from each other. The molar extinction coefficients were 9.8×10^4 at 550 nm, 9.8×10^4 at 537 nm and $1.0 \times 10^5\text{ mol dm}^{-3}\text{ cm}^{-1}$ at 562 nm in chloroform, n-butylacetate and nitrobenzene, respectively. Molybdenum(V)-DPCO complex extracted into these organic solvents was stable for at least 30 min at room temperature.

The plots of $\log D$ vs. $\log$ [HDPCO] at pH 2.5 provided the straight line with a slope of 2.0 for chloroform, n-butylacetate and nitrobenzene. This indicates that the extracted complex may be formulated as $\text{Mo}_2\text{O}_3(\text{DPCO})_4$. DPCO may coordinate to molybdenum(V) through one nitrogen and oxygen atom as a bidentate ligand. The proton-dissociation constant (pK_a) of HDPCO in an aqueous solution was reported to be about 8⁸⁾. The coordination of oxygen atom of HDPCO to molybdenum(V) may facilitate the dissociation of the imino-proton. The acid-strengthening influences on organic ligands produced by metal chelation are frequently large. There are innumerable examples in the literature of complexes of formazans formed by replacement of the imino-proton with a metal ion⁹⁾¹⁰⁾.

Figure 3 shows the pH effect on the extraction of molybdenum(V) with HDPCO into chloroform, nitrobenzene and n-butylacetate. The optimum pH for chloroform, nitrobenzene and n-butylacetate were 2.2, 2.6 and 3.8, respectively. Thus, the extraction curve of the extraction of molybdenum(V) with HDPCO was very similar to that of the extraction of molybdenum(V) with dithizone²⁾. The decrease in the extraction percentage with increasing pH value above the optimum pH may be ascribed to the hydrolysis and the polymerization of molybdenum(V) as is in the case for the extraction of molybdenum(V) with ethylxanthate at a relatively high pH ($\text{pH} > 4$).

Fig. 2 Absorption spectra of molybdenum (V)-DPCO complex.

Organic solvent: (A) chloroform; (B) n-butylacetate; (C) nitrobenzene.

Molybdenum(V)-DPCO, mol dm^{-3} : (A) 4.21×10^{-6} ; (B) 4.01×10^{-6} ; (C) 3.12×10^{-6} .

Fig. 3 Effect of pH on the extraction of molybdenum(V)-DPCO,

Molybdenum(V): $4.89 \times 10^{-5} \text{ mol dm}^{-3}$; HDPCO: $4.99 \times 10^{-3} \text{ mol dm}^{-3}$; Shaking time: 5 min. Organic solvent: (A) chloroform; (B) nitrobenzene; (C) n-butylacetate.

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