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Solvent-extraction Behavior of Molybdenum(VI) with 1,5-Diphenylcarbazone and the Extraction-spectrophotometric Determination of Molybdenum(VI)

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The solvent extraction of molybdenum(VI) with 1,5-diphenylcarbazone (Hdpco) into chloroform, benzene, or tributyl phosphate (tbp) was studied. The molar ratio of molybdenum(VI) : 1,5-diphenylcarbazone in the complex extracted into chloroform or benzene in the range from 1.0 mol dm^{-3} $\mathrm{HNO_3}$ to pH 1.9 was found to be 1 : 2. The extracted complex was estimated to be $\mathrm{MoO_2(dpco)_2}$. On the other hand, molybdenum(VI) may be extracted into tbp as a mixture of $\mathrm{MoO_2(dpco)_2}$ and $\mathrm{MoO_2(dpco)(OH)(tbp)}$. The extraction constants, K_ex $(=[\mathrm{MoO_2(dpco)_2}]_\mathrm{o}/[\mathrm{Mo(OH)_6}][\mathrm{Hdpco}]_\mathrm{o}^2)$, were determined to be 7.9×10^6 and 3.8×10^8 mol^{-2}dm^6 for chloroform and benzene respectively. A black complex formulated as $\mathrm{MoO_2(dpco)_2\cdot5H_2O}$ was formed. Molybdenum(VI) can be determined over the range from 1.50 to 19.0 μg/10 cm^3 within a relative error of ±4%. The interference of diverse ions will be described.

Extraction-spectrophotometric determinations of molybdenum(VI) have been extensively investigated.1) However, there have been few reports describing a detailed extraction behavior of molybdenum(VI) compared to those of other metal ions because of the diversity of molybdenum(VI) species in an aqueous solution. Molybdenum(VI) was extracted as $\mathrm{MoO_2(tta)_2}$ and $\mathrm{HMoO_2(tta)_3}$ with 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione (tta) from 6.0 mol dm^{-3} hydrochloric acid and 0.05 mol dm^{-3} sulfuric acid solutions respectively.2) In some cases, molybdenum(VI) is reduced by chelating extractants with a sulfur atom to give a molybdenum(V) complex.3) Thus, the solvent extraction of molybdenum(VI) is characterized by varied extraction behavior.

1,5-diphenylcarbazone, which has a structure similar to that of 3-mercapto-1,5-diphenylformazan, reacts with a large number of metal ions to form intensively colored complexes. However, because of the poor extractability and instability of the molybdenum(VI)–dpco complex, dpco has not been employed as the extractant for molybdenum(VI). The unstable cadmium(II)- and manganese(II)-dpco complexes in benzene were stabilized by the addition of tbp.4)

The present work describes the extraction behavior of molybdenum(VI) with Hdpco, the preparation of $\mathrm{MoO_2(dpco)_2}$, and the determination of molybdenum(VI).

Experimental

Apparatus. A Hitachi 170-30-type atomic-absorption spectrophotometer was used for the determination of molybdenum(VI). A Hitachi 200-10-type automatic-recording absorption spectrophotometer was used to measure the absorption spectra of molybdenum(VI)–dpco complexes. The pH measurements were made by using a Hitachi-Horiba M-7-type pH meter.

Reagents. *Standard Molybdenum(VI) Solution*: A 0.10-mol dm^{-3} molybdenum(VI) solution was prepared by dissolving 2.419 g of sodium molybdate-water (1/2) (Kanto Co. Ltd.) in 100 cm^3 of a sodium hydroxide solution (pH 9). The working solutions were prepared by diluting the stock solution with redistilled water.

Standard Hdpco Solution: Hdpco (GR. grade, Tokyo Kasei Co., Ltd.) was purified by the method described in the literature.5) A 1.00×10^{-2}-mol dm^{-3} Hdpco solution was prepared by dissolving 0.240 g of Hdpco in 100 cm^3 of an organic solvent.

Organic Solvent: Chloroform, benzene, and tbp of a reagent grade were purified by distillation and then saturated with redistilled water.

All the other reagents were of a guaranteed reagent quality.

Procedure for the Extraction. A 10-cm^3 portion of a 8.00×10^{-5} mol dm^{-3} molybdenum(VI) solution was placed in a 100-cm^3 separatory funnel. To the solution, 10 cm^3 of a given concentration of Hdpco in an organic solvent was added. The pH of the molybdenum(VI) solution was adjusted with nitric acid. The solutions were vigorously shaken for 60, 30, and 10 min for chloroform, tbp, and benzene respectively. After the phases had been allowed to separate, the pH of the aqueous phase was measured. The pH change was negligibly small during the extraction. The distribution ratio of molybdenum(VI) was determined by measuring the molybdenum(VI) in the aqueous phase .

Preparation of $\mathrm{MoO_2(dpco)_2\cdot5H_2O}$. A 400-cm^3 portion of a 0.20-mol dm^{-3} molybdenum(VI) aqueous solution and a 400-cm^3 portion of a 1.0×10^{-2} mol dm^{-3} Hdpco in benzene were placed in a 1-dm^3 separatory funnel. The pH of the molybdenum(VI) solution was adjusted to 2.0 with nitric acid. The solutions were vigorously shaken for 30 min. After the separation, the benzene was distilled out quickly. Black crystals were recrystallized from benzene–heptane (yield, 0.6 g). Found: C, 49.80; N, 17.43; H, 4.20%. Calcd for $\mathrm{MoC_{26}N_8O_7H_{28}}$: C, 49.69; N, 17.82; H, 4.49%.

Procedure for the Determination of Molybdenum(VI). A 10-cm^3 portion of a sample solution containing up to 19.0 μg was placed in a 100-cm^3 separatory funnel. To the solution, 10 cm^3 of 3.00×10^{-3} mol dm^{-3} Hdpco in benzene was then added. The pH of the solution was adjusted to 2.0 before placing the molybdenum(VI) solution in the separatory funnel. The solutions were vigorously shaken for 10 min. After the phase separation, the organic phase was transferred to a 10-mm cell. Within 30 min after the separation, the absorbances of the organic phases were measured at 545 nm against a reagent blank obtained in the same way.

Results and Discussion

Extraction of Molybdenum(VI) with Hdpco. Figure 1 represents the effect of the pH on the extraction of 8.00×10^{-5} mol dm^{-3} molybdenum(VI) with $(1—3)\times10^{-3}$ mol dm^{-3} Hdpco into chloroform. The optimum pH range is 2—3. The extractability decreased on both sides of the optimum pH range. Similar results were obtained for benzene and tbp. For 8.00×10^{-5} mol dm^{-3} molybdenum(VI), the distribution curve of the Mo(OH)$_6$ species[7] was very similar to these extraction—pH curves.

The proton-dissociation constant (pK_a) of Hdpco in an aqueous solution has been reported to be about 8.[8] Under these experimental conditions, all the species of Hdpco distributed in the aqueous phase should exist in a neutral form. The extraction—pH curve shown in Fig. 1 can not be explained by considering the equilibrium of the proton-dissociation of Hdpco in the aqueous phase. The results obtained indicates that a species of Mo(OH)$_6$ other than the molybdenum(VI) species such as Mo(OH)$_5$(H$_2$O)$^+$ and Mo(OH)$_5$O$^-$ is responsible for the extraction of molybdenum(VI) with Hdpco.

The number of molecules of Hdpco involved in the molybdenum(VI)-dpco complex extracted can be obtained from the slope of a plot of log D *vs.* log [Hdpco]$_0$. The result is shown in Fig. 2. The straight lines with the slope of 2.0 suggest that two molecules of Hdpco are involved in the extraction of one molybdenum(VI) atom. Similarly, a straight line with a slope of 2.0 was also obtained for benzene. Thus, the ratio of molybdenum(VI):dpco in the molybdenum(VI)-dpco complex extracted into chloroform and benzene agreed with that of the isolated complex, MoO$_2$(dpco)$_2$. For tbp, on the other hand, the plots of log D *vs.* log [Hdpco] gave straight lines with a slope between 1.2 and 1.7 over the range from 1.0 mol dm^{-3} HNO$_3$ to pH 4.3 (Fig. 3). Molybdenum(VI) may be extracted with Hdpco into tbp as a mixture of MoO$_2$(dpco)$_2$ and MoO$_2$(dpco)(OH)(tbp).

Absorption Spectra of Molybdenum(VI)-dpco Complex. The absorption maximum of isolated MoO$_2$(dpco)$_2$ appeared at 545 nm in chloroform, benzene, or tbp. However, the absorption spectra of the molybdenum-

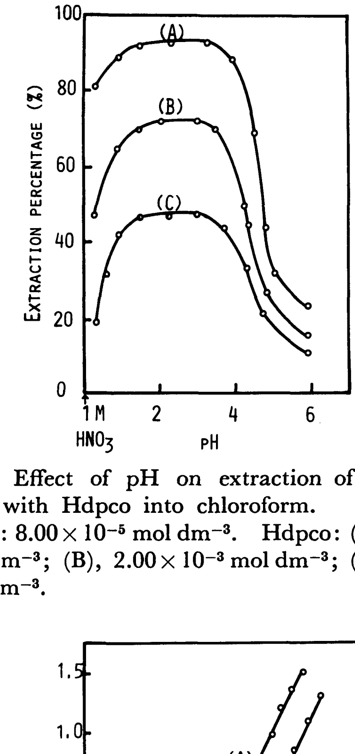

Fig. 1. Effect of pH on extraction of molybdenum(VI) with Hdpco into chloroform.
Mo^{VI}: 8.00×10^{-5} mol dm^{-3}. Hdpco: (A), 3.00×10^{-3} mol dm^{-3}; (B), 2.00×10^{-3} mol dm^{-3}; (C), 1.00×10^{-3} mol dm^{-3}.

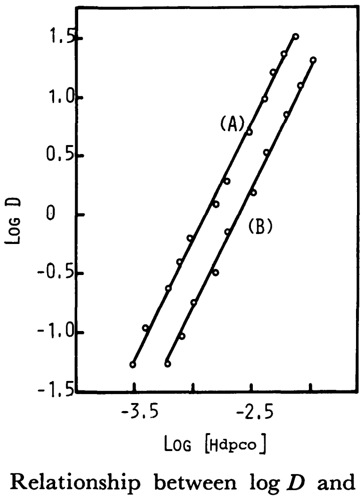

Fig. 2. Relationship between log D and log [Hdpco].
Mo^{VI}: 8.00×10^{-5} mol dm^{-3}. pH: (A) 1.9, (B) 1.0 mol dm^{-3} HNO$_3$. Organic solvent: chloroform.

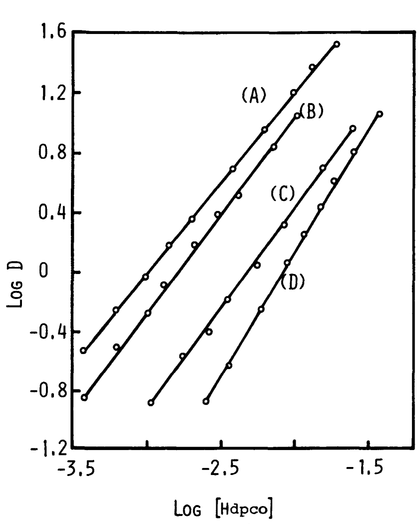

Fig. 3. Relationship between log D and log [Hdpco].
Mo^{VI}: 8.00×10^{-5} mol dm^{-3}. Organic solvent: tbp. pH: (A) 1.9, (B) 1.0, (C) 1.0 mol dm^{-3} HNO$_3$, (D) pH 4.3.

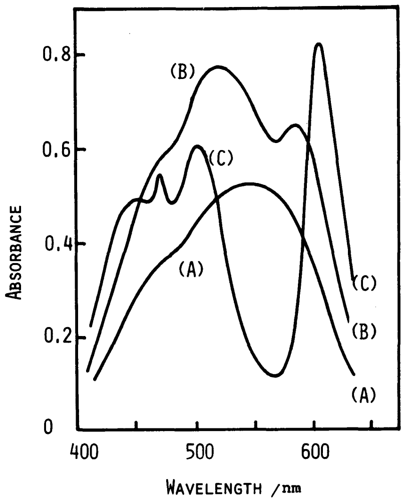

Fig. 4. Absorption spectra of extracted molybdenum(VI)-dpco complex.
Mo^{VI}: 4.00×10^{-5} mol dm^{-3}. HNO$_3$: 0.10 mol dm^{-3}; Organic solvent: chloroform. Hdpco: (A) 1.00×10^{-3} mol dm^{-3}; (B) 1.50×10^{-3} mol dm^{-3}; (C) 3.00×10^{-3} mol dm^{-3}.

(VI)-dpco complex extracted into chloroform depended on the (1—3)$\times 10^{-3}$ mol dm^{-3} Hdpco concentration (Fig. 4) and also on the pH (Fig. 5). The absorption spectrum of the molybdenum(VI) dpco complex extracted with 2.00$\times 10^{-3}$ mol dm^{-3} of Hdpco at pH 2.3 gave the three peaks at 470, 500, and 610 nm. The absorption maximum of the molybdenum(VI)-dpco complex extracted with 3.00$\times 10^{-3}$ mol dm^{-3} of Hdpco into tbp (Fig. 6) and benzene appeared at *ca.* 545 nm. The absorption spectra of the extracted molybdenum(VI)-dpco complex depended on the organic solvent used. The addition of an excess Hdpco to isolated $MoO_2(dpco)_2$ in chloroform, benzene, or tbp caused an absorption spectral change, giving spectra similar to those of the molybdenum(VI)-dpco complex extracted with 3.00$\times 10^{-3}$ mol dm^{-3} of Hdpco. This abnormal absorption spectral behavior probably results from the reaction of the extracted $MoO_2(dpco)_2$ with free Hdpco in the organic phase. The structure and composition of the molybdenum(VI)-dpco complex extracted with a large excess of Hdpco were not ascertained.

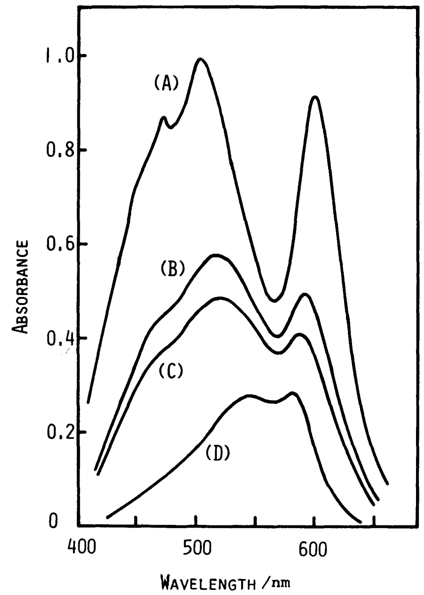

Fig. 5. Absorption spectra of extracted molybdenum (VI)-dpco complex.
Mo^{VI}: 4.00$\times 10^{-5}$ mol dm^{-3}. Hdpco: 2.00$\times 10^{-3}$ mol dm^{-3}; Organic solvent: chloroform. pH (A) 2.3; (B) 1.0 mol dm^{-3} HNO_3, (C) 4.5; (D) 5.0.

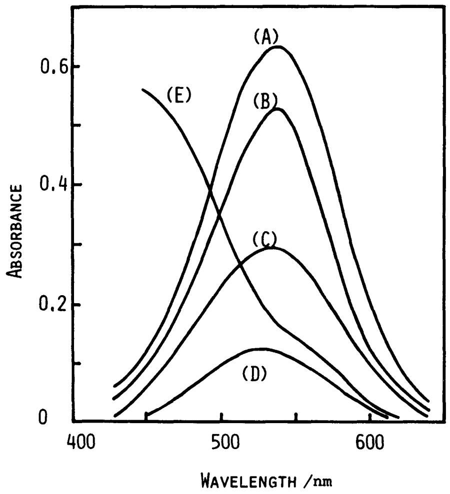

Fig. 6. Absorption spectra extracted molybdenum(VI)-dpco complex into tbp and 1.00$\times 10^{-3}$ mol dm^{-3} Hdpco (E).
Mo^{VI}: 2.00$\times 10^{-5}$ mol dm^{-3}. Hdpco: 3.00$\times 10^{-3}$ mol dm^{-3}. pH: (A) 1.9; (B) 0.30 mol dm^{-3} HNO_3; (C) 1.0 mol dm^{-3} HNO_3; (D) 4.4.

In general, molybdenum(VI) complexes of organic ligands involve a *cis*-MoO_2^{2+} structure.[9,10] A *cis*-MoO_2^{2+} structure for $MoO_2(dpco)_2$ may be proposed in spite of the lack of any direct proof supporting a *cis*-structure.

Extraction Constant for the Extraction of Mo(OH)$_6$ with Hdpco. As has been mentioned above, $Mo(OH)_6$ would be a more reactive species toward Hdpco than $Mo(OH)_5(H_2O)^+$ and $Mo(OH)_5O^-$, which exist at pH 2.0. At the optimum pH of 1.9—2.5, molybdenum(VI) is present predominantly as $Mo(OH)_6$.[7] Therefore, the equation which best represents the extraction equilibrium at pH 2.0 is perhaps:

$$Mo(OH)_6 + 2Hdpco \overset{K_{ex}}{\rightleftharpoons} MoO_2(dpco)_2,$$

with the extraction constant:

$$K_{ex} = \frac{[MoO_2(dpco)_2]_o}{[Mo(OH)_6][Hdpco]_o^2},$$

where the subscript o refers to the organic phase. The values of K_{ex} for chloroform and benzene were determined to be 7.9$\times 10^6$ and 3.8$\times 10^8$ mol^{-2} dm^6, respectively at 20 °C. The value of K_{ex} for benzene was about 50 times that for chloroform. It was also found that the extractability of the molybdenum(VI)-dpco complex into chloroform was better than that into tbp, though the K_{ex} for tbp was not determined.

Back-extraction of Molybdenum(VI)-dpco Complex. The back-extraction of the molybdenum(VI)-dpco complex extracted into chloroform, benzene, or tbp with aqueous solutions of various pHs was studied by the following procedure. Ten cm^3 of a molybdenum(VI)-dpco complex solution, which had

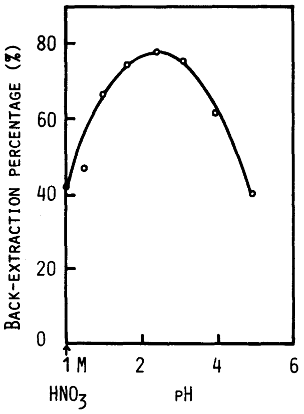

Fig. 7. Effect of pH on back-extraction of molybdenum(VI)-dpco complex extracted into chloroform.
Mo^{VI}: 8.00$\times 10^{-5}$ mol dm^{-3}. Hdpco: 2.00$\times 10^{-3}$ mol dm^{-3}. pH values were adjusted by using nitric acid solution.

been prepared by shaking 8.00×10^{-5} mol dm^{-3} of molybdenum(VI) solution with 2.00×10^{-3} mol dm^{-3} of Hdpco in an organic solvent at pH 1.9, was shaken with 10-cm^3 portions of aqueous solutions of various pHs for 60 min. The results are shown in Fig. 7. The back-extraction—pH curve, was quite similar to that of the forward-extraction—pH curve, indicating that the extraction equilibrium is reversible. For benzene and tbp, similar results were obtained.

Infrared Spectrum of $MoO_2(dpco)_2$. The infrared spectrum of $MoO_2(dpco)_2$ was distinctly different from that of Hdpco. The free Hdpco showed the strong band assigned to the carbon–oxygen vibration at 1705 cm^{-1}. In the case of $MoO_2(dpco)_2$, the band of the carbon–oxygen vibration disappeared completely. The dpco in $MoO_2(dpco)_2$ must be present in the enol configuration. The infrared spectrum of $MoO_2(dpco)_2$ was quite similar to that of $Cr(dpco)(H_2O)_4^{2+}$.[11] The three weak bands at 620, 610, and 595 cm^{-1} for $Cr(dpco)(H_2O)_4^{2+}$ were ascribed to the vibrational chromium–oxygen band.[6] The two weak bands at 600 and 630 cm^{-1} for $MoO_2(dpco)_2$ may be assigned to the vibrational molybdenum–oxygen bands. The molybdenum(V) oxo complexes of 2-methyl-8-quinolinol, $(C_{10}H_8NO)_4Mo_2O_3$, $(C_{10}H_8NO)_2MoO(OH)$, and $(C_{10}H_8NO)_2Mo_2O_4$, showed vibrational molybdenum–oxygen bands at 932—945, 935—945, and 930—945 cm^{-1} respectively.[11] The strong broad band between 900 and 940 cm^{-1} for $MoO_2(dpco)_2$ may be assigned to the molybdenum–oxygen stretching.

Determination of Molybdenum(VI). Molybdenum(VI) was determined based on the foregoing procedure. The method obeyed Beer's law at molybdenum(VI) concentrations from 1.50 to 19.0 μg/10 cm^3, within a relative error of ±4%. The molar extinction coefficient was 5.1×10^4 dm^3 mol cm^{-1} at 545 nm. The effects of various metal ions on the determination of 9.6 μg/10 cm^3 molybdenum(VI) were also examined. The presence of such metal ions as cobalt(II), zinc(II), nickel(II), manganese(II), lead(II), and tungsten(VI) can be tolerated in amounts up to 2.5×10^2 μg/10 cm^3, within a relative error of ±5%. The presence of amounts of iron(III), tin(II), and zirconium(IV) equal to that of molybdenum(VI) can be tolerated below a relative error of 5%. The interference of 20 μg/10 cm^3 of copper(II) can be masked in the presence of 0.01 mol dm^{-3} of sodium hydrogensulfite. The present method was more sensitive than the thiocyanate method[12], the dithiol method[13], the oxinate method[14], and the flavon-3-ol-2′-sulfonate method[10], but less sensitive than the pyrogallol red method[15] and 3,4-dihydroxyazobenzene method.[16]

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