Extraction Behavior of Di-μ-oxo-bis[oxomolybdenum(V)] with 2-Methyl-5-octyloxymethyl-8-quinolinol

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Binuclear oxomolybdenum(V), $Mo_2O_4^{2+}$, was quantitatively extracted with 0.01 mol dm^{-3} 2-methyl-5-octyloxymethyl-8-quinolinol (HMO_8Q) in chloroform at pH 2.3 and isobutyl methyl ketone at pH 1.0—3.9. To elucidate the extraction equilibrium, the effect of the pH as well as the HMO_8Q and molybdenum(V) concentration on the distribution ratio of $Mo_2O_4^{2+}$ was studied. The extracted complex was found to be $Mo_2O_4(MO_8Q)_2$; the extraction constants (K_{ex}) were determined to be $10^{0.15}$ and $10^{1.57}$ in benzene and chloroform, respectively. These values were lower than $K_{ex}=10^{3.26}$ obtained in the $Mo_2O_4^{2+}$-5-octyloxymethyl-8-quinolinol–chloroform system, suggesting a steric effect of the methyl group at the 2-position. In the presence of trioctylphosphine oxide (TOPO) a great enhancement of molybdenum(V) extraction was found and could be ascribed to the formation of an adduct, $Mo_2O_4(MO_8Q)_2(TOPO)$.

Since molybdenum is among the important biological elements, there have been many reports on the analytical research of molybdenum. The solvent extraction of molybdenum(VI) has been extensively studied with various chelating extractants, such as α-hydroxyoximes[1] and 8-quinolinols.[2—5] The present authors have investigated the separation of molybdenum(VI) with long-chain alkylated 8-quinolinol derivatives, such as 5-octyloxymethyl-8-quinolinol (HO_8Q), 2-methyl-5-octyloxymethyl-8-quinolinol (HMO_8Q), and 5-(4-nitrophenylazo)-7-(4-ethyl-1-methyloctyl)-8-quinolinol (HNEQ).[5] In that study, HMO_8Q was found to be superior to HO_8Q and HNEQ in spite of the lower extraction constant of HMO_8Q, because it demonstrated adequate selectivity toward molybdenum(VI) in acidic solutions and easy stripping of molybdenum(VI) with a diluted aqueous ammonia solution.

On the other hand, little attention has been focused on the extraction of molybdenum(V). One of the present authors has studied the extraction behavior of molybdenum(V) with different types of extractants, and compared it with that of molybdenum(VI). For example, diphenylcarbazone[6] reacts with molybdenum(V) and molybdenum(VI) to give extractable complexes, while 3-mercapto-1,5-diphenylformazane (dithizone) forms an extractable complex with molybdenum(V), but not with molybdenum(VI).[7] In the dithizone case, tributylphosphate (TBP) was a better solvent because of its coordination ability to the molybdenum(V)–dithizone complex. Ethylxanthate extracts molybdenum(VI) to yield a molybdenum(V)–ethylxanthate complex.[6] Thus, the extraction behavior of molybdenum(V,VI) fairly depends on the kinds of extractants. Recently, one of the authors also reported that molybdenum(V) was extracted with HO_8Q in chloroform as two types of molybdenum(V) complexes, $Mo_2O_4(O_8Q)_2$ at pH 1.0 and $Mo_2O_3(O_8Q)_4$ at pH 2.5, which were identified by the absorption spectra of the organic phase.[4] However, details concerning the extraction of molybdenum(V) have remained unclear.

In the present work, the alkylated 2-methyl-8-quinolinol derivative, HMO_8Q, was applied to an extraction-equilibrium study of binuclear oxomolybdenum(V), $Mo_2O_4^{2+}$. The effects of organic solvents and such variables as the pH and HMO_8Q concentration on the extraction of molybdenum(V) were studied. Also, the composition of the extracted complex and the extraction constant were determined in chloroform and benzene. The result in the chloroform system was compared with that of HO_8Q in order to clarify the effect of the 2-methyl groups on the extraction separation of molybdenum(V) with 8-quinolinol derivatives. Moreover, since the highest extraction efficiency was given by isobutyl methyl ketone (MIBK), which is a solvating solvent, the effect of a synergistic ligand, such as trioctylphosphine oxide (TOPO), was studied in benzene and chloroform.

Experimental

Reagents. HMO_8Q was synthesized by the reaction of 2-methyl-5-chloromethyl-8-quinolinol with 1-octanol, as described previously.[8] Chloroform was washed with a 0.1% hydroxylamine solution and then deionized water before use. Benzene was purified by distillation.

A standard solution of molybdenum(VI) was purchased and used as the calibration standard for inductively coupled plasma atomic emission spectrometry (ICP-AES). Other chemicals were of guaranteed reagent grade and were used as received.

Preparation of Binuclear Oxomolybdenum(V). A stock solution of $Mo_2O_4^{2+}$ was prepared according to a method based on two references.[9,10] Sodium molybdate (8.2 g) was dissolved in 10 mol dm^{-3} HCl (180 cm^3), mixed with hydrazine hydrochloride (6.6 g), and heated for 2—3 h at 80 °C. The solution was first filtered and then concentrated with a rotary evaporator at 40—50 °C until dark-green precipitates appeared. These were dissolved in a small amount of 10 mol dm^{-3} HCl and filtered. The filtrate was diluted 200 times with deionized water and transferred to a Dowex 50W-X12 cation exchange column (12-cm height, 1.6-cm diameter). A brown band consisting of $Mo_2O_4^{2+}$ was retained on the column, washed with 0.2 mol dm^{-3} HCl, and then eluted with 2 mol dm^{-3} HCl or $HClO_4$. The stock solution of $Mo_2O_4^{2+}$ was stored at 0 °C under a nitrogen atmosphere.

Extraction Procedure. An aqueous solution containing 3×10^{-7}—3×10^{-5} mol dm^{-3} $Mo_2O_4^{2+}$ and 0.10 mol dm^{-3} (H, Na)Cl was shaken with an equal volume of an organic solution of 2×10^{-3}—4×10^{-2} mol dm^{-3} HMO$_8$Q for between 10 min and 5 h at 25 °C. After phase separation, the molybdenum(V) in the aqueous phase was determined by ICP-AES. Molybdenum(V) extracted into the organic phase was stripped with a 0.1 mol dm^{-3} aqueous ammonia solution and determined by ICP-AES. The distribution ratio (D) was calculated based on the molybdenum(V) concentration in each phase. The pH of the aqueous phase was adjusted with a 1×10^{-3} mol dm^{-3} acetate or a 1×10^{-3} mol dm^{-3} piperazine-*N*,*N'*-bis(2-ethanesulfonate) buffer solution. The equilibrium pH value of the aqueous phase was measured with a glass electrode just after phase separation.

Results and Discussion

Several methods for preparing molybdenum(V) have been proposed. Sasaki et al. used hydrazine hydrochloride as a reducing agent for molybdenum(VI) and pyridine (py) to precipitate molybdenum(V) as $(Hpy^+)_2(MoOCl_5^{2-})$.[10] According to their method, however, the complete removal of pyridine from the molybdenum(V) solution was not easy using a cation exchange column. Hence, a modified method (described in the experimental section) was adopted to prepare a molybdenum(V) stock solution.

The absorption spectra of the molybdenum(V) solution were measured in 2 mol dm^{-3} $HClO_4$ and in 0.10 mol dm^{-3} (H, Na)Cl at pH 1.86. The absorption maxima, λ_{max}/nm (and molar absorptivities, ε/mol^{-1} dm^3 cm^{-1}), were 383 (76), 295 (3400), and 257 (4000) in 2 mol dm^{-3} $HClO_4$ and 378 (76), 295 (3400), and 255 (3900) at pH 1.86. These are in good agreement with those reported by Ardon and Pernick:[11] 293 (3454) and 254 (3998) in 2 mol dm^{-3} $HClO_4$ and Sasaki and Sykes:[9] 384 (103), 295 (3546), and 255 (4320) in 2 mol dm^{-3} $HClO_4$. From these results, it is concluded that molybdenum(V) exists as $Mo_2O_4^{2+}$ in 0.1 mol dm^{-3} (H, Na)Cl solutions, as proposed in the literature.

Extraction Behavior and Equilibrium. The extraction of molybdenum(V) with 0.01 mol dm^{-3} HMO$_8$Q was carried out by shaking for 1 h. Figure 1 shows the extraction curves of molybdenum(V) in chloroform, benzene, and MIBK systems. A quantitative extraction was observed in chloroform at pH 2.3 and in MIBK at pH 1.0—3.9, while ca. 95% was extracted in benzene at pH 2.5—4.0. The percentage extraction below pH 2 decreased in the following order: MIBK > chloroform > benzene. Since the highest extraction was given by MIBK, which is a representative solvating solvent, the molybdenum(V)–MO$_8$Q complex probably forms adducts with MIBK as a Lewis base in the organic phase. This idea is supported by the adduct formation of TOPO, as is described later. Although the difference between chloroform and benzene cannot be explained based on any experimental evidence at the present time, we point out the hydrogen bonding ability of chloroform as a donor[12] and 8-quinolinol complexes as an acceptor.[13]

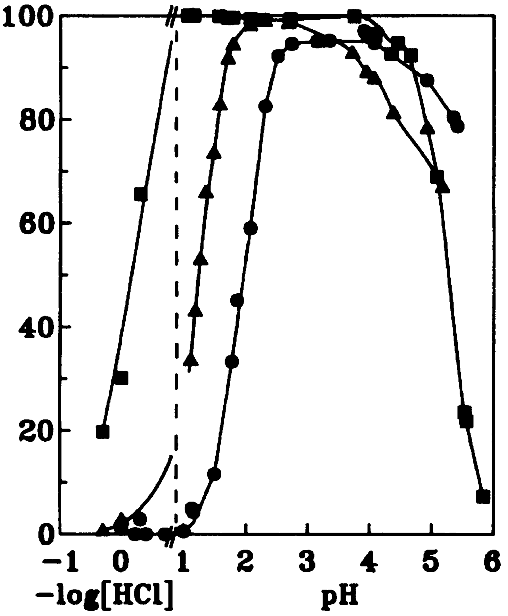

Fig. 1. Extraction of molybdenum(V) with 0.010 mol dm^{-3} HMO$_8$Q in benzene (●), chloroform (▲), and MIBK (■).

In the higher pH region, the extractability of molybdenum(V) decreased with increasing pH in all of the solvent systems. A similar pH dependence was observed in the extraction of molybdenum(V) with diphenylcarbazone,[6] ethylxanthate,[6] and dithizone[7] in several organic solvents. This phenomenon may be due to the hydrolysis or polymerization of $Mo_2O_4^{2+}$ in the aqueous phase, though there is no other information available concerning the reaction. Additional experiments were not carried out in this pH region.

The extraction equilibrium of molybdenum(V) with HMO$_8$Q in chloroform and benzene was investigated in the pH region of 1 to 2.5. The distribution ratios obtained from the forward and backward extractions at pH 1.3 became constant within 30 min of the shaking time. The rapid attainment of equilibrium is understandable from the labile property of $Mo_2O_4^{2+}$

species.[9,10] The relationship between $\log D$ and pH is shown in Fig. 2. The agreement of the distribution ratio from the forward extraction with that from the backward extraction certifies the attainment of the extraction equilibrium with the given pH range. Using a least-squares method, the slopes of the plots in Fig. 2 were obtained to be 2.1 and 1.8 for chloroform and benzene, respectively. This suggests that two protons are released from the HMO_8Q molecules per extractable molybdenum(V) complex.

As is mentioned below, molybdenum(V)–2-methyl-8-quinolinol (MQ) complexes have been reported to give three types of compositions, such as $Mo_2O_3(MQ)_4$, $Mo_2O_4(MQ)_2$, and $MoO(OH)(MQ)_2$.[14] Hence, we examined whether the dimeric form of $Mo_2O_4^{2+}$ in the aqueous phase was altered to the monomeric or other polymeric forms during extraction or not. Figure 3 shows the effect of the molybdenum(V) concentration on extraction with HMO_8Q in chloroform. The extraction was found to be independent of the molybdenum(V) concentration in the organic phase at pH 1.25 and at pH 1.49—1.52. This was also true in the case of benzene. These results mean that the molybdenum(V) species in the organic phase has the same dimeric form as that in the aqueous phase.

The effect of the HMO_8Q concentration on the extraction of molybdenum(V) was investigated in the chloroform and benzene system at pH 1.33 and 1.93, respectively. Figure 4 shows plots of $\log D$ vs. $\log\,[HMO_8Q]_o$, which give straight lines with slopes of 1.9 and 2.0 for chloroform and benzene, respectively. These results indicate that two molecules of MO_8Q bind to a binuclear molybdenum(V) complex. Compared with the composition of the molybdenum(V)–MQ complexes reported,[14] i.e., $Mo_2O_3(MQ)_4$, $Mo_2O_4(MQ)_2$, and $MoO(OH)(MQ)_2$, the extracted complex can be concluded to be $Mo_2O_4(MO_8Q)_2$.

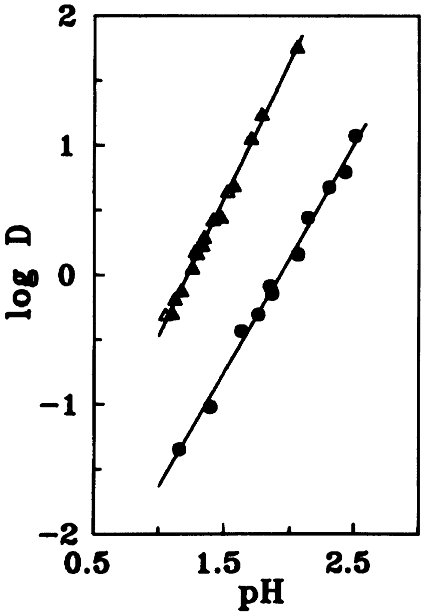

Fig. 2. Effect of pH on the extraction of molybdenum(V) with 0.010 mol dm^{-3} HMO_8Q in benzene (●) and chloroform (▲ △). Solid symbols, forward extraction; open symbols, backward extraction.

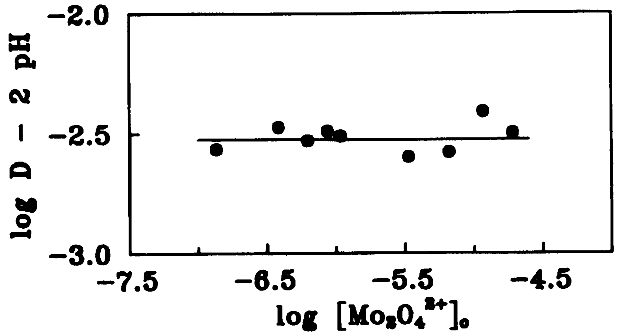

Fig. 3. Effect of the molybdenum(V) concentration in chloroform on the extraction with 0.010 mol dm^{-3} HMO_8Q at pH 1.25 (for 1.4×10^{-7}—1.1×10^{-6} M $Mo_2O_4^{2+}$) and at pH 1.49—1.52 (for 3.4×10^{-6}—1.9×10^{-5} M $Mo_2O_4^{2+}$).

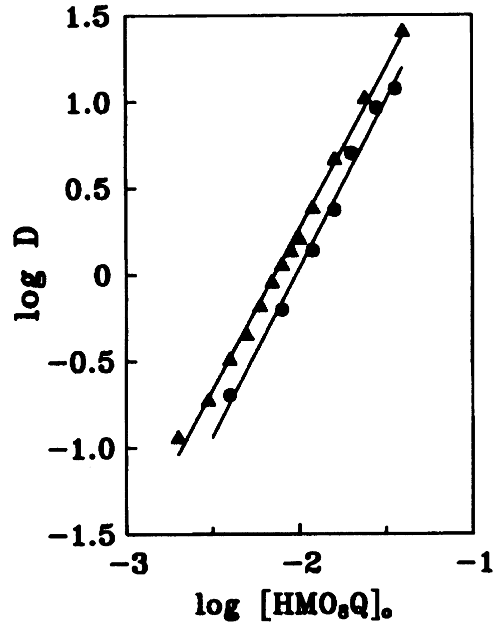

Fig. 4. Effect of the HMO_8Q concentration in benzene (●) and chloroform (▲) on the distribution ratio of molybdenum(V) at pH 1.93 and pH 1.33, respectively.

This composition of the molybdenum(V)–MO_8Q complex was further confirmed spectrophotometrically after the extraction of 1.8×10^{-4} mol dm^{-3} molybdenum(V) with 1.0×10^{-2} mol dm^{-3} HMO_8Q in chloroform at pH 2.01. In the absorption spectrum of the extracted complex, λ_{max} (ε) and the shoulder (ε) appeared at 388 (12000) and 740 (110), respectively. The absorption spectra of the molybdenum(V)-2-methyl-8-quinolinol complexes synthesized have been reported as follows:[14] The values of λ_{max} (ε)

were 350 (12012) and 700 (275) for $Mo_2O_4(MQ)_2$; 350 (17800), 540 (708), and 750 (54) for $Mo_2O_3(MQ)_4$; 354 (3894), 545 (548), and 752 (33) for $MoO(OH)(MQ)_2$. As a result, the spectrum of the extracted molybdenum(V)–MO_8Q complex is similar to that of $Mo_2O_4(MQ)_2$, supporting the formation of $Mo_2O_4(MO_8Q)_2$.

In a previous study for molybdenum(V)–HO_8Q, two types of the molybdenum(V) complexes, $Mo_2O_4(O_8Q)_2$ and $Mo_2O_3(O_8Q)_4$, were found.4) In the present study, however, a single species, $Mo_2O_4(MO_8Q)_2$, was identified in the organic phase. The $Mo_2O_4(O_8Q)_2$ molecule has one O_8Q ligand per one molybdenum(V) atom, while the $Mo_2O_3(O_8Q)_4$ has the two ligands per one molybdenum(V). In the HMO_8Q case, if two MO_8Q ligands bind to one molybdenum(V) atom, a steric repulsion may occur between the 2-methyl group of one MO_8Q ligand and another ligand or the oxo groups bound to molybdenum(V) because of the relatively small ionic radius of molybdenum(V) (61 pm15)).

From the results described above, the extraction reaction of molybdenum(V) with HMO_8Q can be expressed as

$$Mo_2O_4^{2+} + 2HMO_8Q_o \rightleftharpoons Mo_2O_4(MO_8Q)_{2,o} + 2H^+, \quad (1)$$

where the subscript (o) denotes the organic phase. The partition coefficient of HMO_8Q between chloroform and water was estimated to be as high as $10^{7.4}$.5) In addition, the acid-dissociation constants for $H_2MO_8Q^+$ and HMO_8Q are expected to be close to those of MQ, since the alkyl groups of HOnQ (n=1—6) scarcely influenced the acid-dissociation constants.16) Therefore, the HMO_8Q concentration in an aqueous phase at pH 1—2.5 is negligibly low. The HMO_8Q concentration in the organic phase can be approximately the same as the initial concentration in the organic phase.

If the distribution ratio of $Mo_2O_4^{2+}$ can be written as $D=[Mo_2O_4(MO_8Q)_2]_o/[Mo_2O_4^{2+}]$, it can be expressed using the equilibrium constant for Eq. 1 (extraction constant, K_{ex}) as follows:

$$\log D = \log K_{ex} + 2\log{[HMO_8Q]_o} + 2\ pH. \quad (2)$$

Equation 2 reasonably explains the results given in Figs. 2, 3, and 4.

The values of $\log K_{ex}$ for chloroform and benzene were calculated using Eq. 2, and are shown in Table 1. The errors are one standard deviation for the averages. To understand the effect of the 2-methyl group of the 8-quinolinol derivatives, the $\log K_{ex}$ value for molybdenum(V)–HO_8Q–chloroform was calculated to be 3.26 from the $\log D$ vs. $\log{[HO_8Q]_o}$ plots at pH 1.0 reported previously.4) The extraction constant for HMO_8Q was lower than that for HO_8Q by a factor of 47. On the other hand, in the molybdenum(VI) case,5) the extraction constant (defined by $K_{ex}=[MoO_2(MO_8Q)_2]_o[MoO_4^{2-}]^{-1}[H^+]^{-2}[HMO_8Q]_o^{-2}$) for HMO_8Q was lower than that for HO_8Q by a factor of 660. The difference in the effect of the 2-methyl group on the extraction of molybdenum(V) and molybdenum(VI) can be similarly explained by the structure of the complexes, as described for the two types of binuclear oxomolybdenum(V) complexes. In the molybdenum(VI)–MO_8Q complex, two MO_8Q molecules coordinate the molybdenum(VI) atom of MoO_2^{2+} and may cause a greater steric effect of the 2-methyl groups than that in $Mo_2O_4(MO_8Q)_2$.

Table 1. Equilibrium Constants for the Extraction of $Mo_2O_4^{2+}$ with HMO_8Q and TOPO at 0.10 mol dm^{-3} (H, Na)Cl and 25 °C

Solvent	$\log K_{ex}$	$\log \beta_1$	$\log K_{ex,s,1}$
C_6H_6	0.15±0.10	3.20±0.09	3.4 ±0.1
$CHCl_3$	1.57±0.08	1.32±0.04	2.89±0.09

Effect of Trioctylphosphine Oxide. The extraction of molybdenum(V) with HMO_8Q in MIBK demonstrated a higher extraction efficiency than that in chloroform and benzene. This solvent effect is probably related to the adduct formation of $Mo_2O_4(MO_8Q)_2$ with MIBK molecules. Hence, a further investigation of the effect of TOPO, which is a stronger Lewis base, was carried out.

The extraction efficiency of $Mo_2O_4^{2+}$ with HMO_8Q was greatly enhanced by TOPO, as expected. The synergistic effect can be evaluated from D'/D, where D is the distribution ratio of molybdenum(V) without TOPO, and D' is that in the presence of TOPO. Figure 5 shows that $\log{(D'/D)}$ increases along with an increase in the TOPO concentration. This phenomenon should be ascribed to the adduct formation of $Mo_2O_4(MO_8Q)_2$ with TOPO in the organic phase.

The synergistic extraction can be written as

$$\begin{aligned} &Mo_2O_4^{2+} + 2HMO_8Q_o + m\mathrm{TOPO}_o \\ &\quad \rightleftharpoons Mo_2O_4(MO_8Q)_2(\mathrm{TOPO})_{m,o} + 2H^+. \end{aligned} \quad (3)$$

The distribution ratio (D') of $Mo_2O_4^{2+}$ is written as

$$\begin{aligned} D' &= \frac{[Mo_2O_4(MO_8Q)_2]_o + \sum[Mo_2O_4(MO_8Q)_2(\mathrm{TOPO})_m]_o}{[Mo_2O_4^{2+}]} \\ &= \frac{[Mo_2O_4(MO_8Q)_2]_o(1+\sum\beta_m[\mathrm{TOPO}]_o{}^m)}{[Mo_2O_4^{2+}]}, \end{aligned} \quad (4)$$

where β_m ($=[Mo_2O_4(MO_8Q)_2(\mathrm{TOPO})_m]_o[Mo_2O_4(MO_8Q)_2]_o^{-1}[\mathrm{TOPO}]_o^{-m}$) is the overall adduct formation constant in the organic phase. The synergistic enhancement of the distribution ratio (D'/D) is expressed as

$$D'/D = 1+\sum\beta_m[\mathrm{TOPO}]_o{}^m. \quad (5)$$

If $Mo_2O_4(MO_8Q)_2(\mathrm{TOPO})_m$ is the predominant species in the organic phase, Eq. 5 can be rewritten as

$$\log{(D'/D)} = \log \beta_m + m\log{[\mathrm{TOPO}]_o}. \quad (6)$$

As shown in Fig. 5, the plot of $\log{(D'/D)}$ vs. $\log{[\mathrm{TOPO}]_o}$ in the benzene system gives a straight line

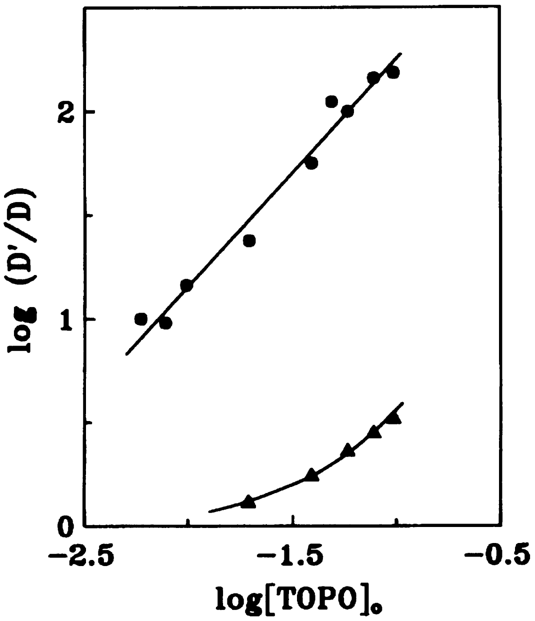

Fig. 5. Effect of the TOPO concentration on the synergistic enhancement of the extraction of molybdenum(V) with 0.010 mol dm^{-3} HMO_8Q in benzene (●) at pH 1.64 and chloroform (▲) at pH 1.26.

with a slope of 1.1±0.1. The adduct contains at least one TOPO molecule, that is, the predominant species of the adduct should be $Mo_2O_4(MO_8Q)_2(TOPO)$ at the TOPO concentration range of 0.01—0.1 mol dm^{-3}. Considering the structure of $Mo_2O_4^{2+}$ in solutions,[9,10] the extracted complex, $Mo_2O_4(MO_8Q)_2$, might have two water molecules weakly bound to molybdenum(V). Consequently, one TOPO molecule can coordinate to a molybdenum(V) atom by replacing the water molecule.

Compared with the benzene system, the enhancement effect of TOPO in chloroform was markedly low. Since the slope of the $\log(D'/D)$ vs. $\log[\mathrm{TOPO}]_o$ plot is lower than unity, even at 0.1 mol dm^{-3} of TOPO, there are two species, $Mo_2O_4(MO_8Q)_2$ and $Mo_2O_4(MO_8Q)_2(TOPO)$, in the organic phase. Therefore, the adduct formation constant was calculated using Eq. 5 as $m=1$. The synergistic extraction constant ($K_{\mathrm{ex,s},m}$) for Eq. 3 was obtained using the relation, $K_{\mathrm{ex,s,1}}=K_{\mathrm{ex}}\beta_1$. Those values are listed in Table 1 along with the standard deviations. $K_{\mathrm{ex,s,1}}$ in the benzene system is larger than that in chloroform, owing to the larger adduct formation constant in benzene. The lowering of the adduct formation constant in chloroform is ascribable to a decrease in the activity of TOPO due to the interaction between chloroform and TOPO.

The capability of HMO_8Q for the extraction and separation of molybdenum(V) was evaluated by comparing those of other extractants reported so far. A quantitative extraction of molybdenum(V) has been achieved only by 0.01 mol dm^{-3} HMO_8Q in chloroform at pH 2.3 and MIBK at pH 1—3.9 in the present work or 3×10^{-4} mol dm^{-3} dithizone in TBP at pH 3.2.[7] Furthermore, the extraction separation of molybdenum(V) and molybdenum(VI) is also possible with HMO_8Q. That is, molybdenum(VI) is quantitatively extracted with 0.01 mol dm^{-3} HMO_8Q in benzene from the acidic solutions up to 0.5 mol dm^{-3} HCl,[5] whereas, molybdenum(V) is not extracted at all from 0.1—1 mol dm^{-3} HCl. Therefore, molybdenum(VI) can be readily separated from molybdenum(V) at 0.1—0.5 mol dm^{-3} HCl. A similar extraction separation of molybdenum(VI) from molybdenum(V) can be expected with HO_8Q in stronger acid solutions up to 5 mol dm^{-3}.[4] The selective extraction of molybdenum(V) is given by dithizone in TBP because of no extractability of molybdenum(VI).

On the other hand, it is very important to strip the molybdenum complexes from the organic phase to proper aqueous solutions for practical use. In the HMO_8Q case, although molybdenum(V) as well as molybdenum(VI) could be readily stripped with a diluted aqueous ammonia solution, this was only partially true in the HO_8Q case. Consequently, HMO_8Q is a more excellent extractant for molybdenum(V, VI) than is HO_8Q.

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