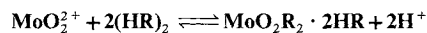# EXTRACTION EQUILIBRIUM OF MOLYBDENUM(VI) WITH 2-ETHYLHEXYL PHOSPHONIC ACID MONO-2-ETHYLHEXYL ESTER

YOSHINOBU SATO, FERNANDO VALENZUELA, TERUO TSUNEYUKI, KAZUO KONDO AND FUMIYUKI NAKASHIO

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The extraction equilibrium of molybdenum(VI) from nitric, hydrochloric and sulfuric acid solution with 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester dissolved in n-heptane was examined at 303 K. It was clarified that molybdenum(VI) was extracted with the extractant (HR) according to the following equation, in low concentration range of the metal.

$$MoO_2^{2+} + 2(HR)_2 \rightleftharpoons MoO_2R_2 \cdot 2HR + 2H^+$$

The extraction equilibrium constants were obtained. The experimental results were interpreted quantitatively by taking account of the equilibrium concentration of a cationic species of molybdenum(VI) in aqueous solution.

Introduction

Solvent extraction technology has become increasingly important in the recovery of rare metals from the viewpoint of the conservation of energy and material resources. Rare metals which possess physically and chemically specific properties are applied in many fields of advanced technology. Since rare metals are considered to be increasingly in great demand for the future, it is desired to study the selective separation and concentration of these metals.

Molybdenum, which is used in alloys, as a catalyst and so on, is mainly collected as molybdenite (MoS_2), a valuable by-product of copper mining, and thus the separation of this metal from copper is of importance.[4] Solvent extraction was recently applied to industrial processes for the recovery of molybdenum and tungsten.[5,8,9]

Diverse molybdate species have been reported to exist in aqueous solution.[1,7,16,17] Generally, the hexavalent form of molybdenum is the most stable in aqueous solution, but since it tends to be hydrolyzed and to form polyhetero acids, identification is not always possible. It is well known that in aqueous solution a series of polymolybdate anions predominate in the region of pH greater than 2 and that molybdenum forms cationic species only at a low pH. These facts make a quantitative treatment of the extraction equilibrium very complicated. Most studies of the extraction of molybdenum so far have been qualitative, using such extractants as high-molecular weight tertiary alkylamines[6,10,18] such as tri-n-octylamine and Aliquat 336, di(2-ethylhexyl) phosphoric acid[3,21] (henceforth referred to as D2EHPA), tri-n-butyl phosphate,[19] sulfoxides,[2] β-hydroxy-oximes[11] and 2-thenoyltrifluoroacetone.[15]

In the present study, the extraction equilibrium of molybdenum(VI) with 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (henceforth referred to as PC-88A, its commercial name, abbreviated as HR) was examined at 303 K in nitric acid, hydrochloric acid and sulfuric acid media and the extraction equilibrium constant was determined for each acid solution. The experimental results were interpreted quantitatively by taking account of the chemical species of molybdenum(VI) in aqueous solution. A possible mechanism of the extraction was deduced from the experimental results.

1. Experimental

PC-88A was used as delivered from Daihachi Chemical Industry Co. Ltd., (Lot. No. B60502), since its purity (95.5%) could not be improved significantly by the usual method reported with respect to D2EHPA.[12,14] The organic solution was prepared by dissolving PC-88A in n-heptane of commercial GR grade. The aqueous solution was prepared by dissolving sodium molybdate dihydrate in deionized water and adjusting pH with each acid mentioned above with normality of 1000 mol/m³ and 1000 mol/m³ sodium hydroxide in the region of pH < 2.5, or 100 mol/m³ sodium hydroxide in the region of

pH > 2.5. The inorganic reagents used were commercial GR grade. The experimental conditions used were as follows. The initial concentration of each species was, for the molybdenum, $C_{Mo,0} = 0.1$–10 mol/m^3; and for the extractant, $C_{(HR)_2,0} = 0.5$–100 mol/m^3.

Aqueous and organic solutions of equal volumes (20 cm^3) were mixed in a flask and shaken at 303 K to attain extraction equilibrium. After that, the two phases were separated and each phase was removed by pipette for analysis. Molybdenum concentration in the aqueous solution was determined by a Shimadzu AA646 atomic absorption spectrophtometer with a N$_2$O/C$_2$H$_2$ flame. The concentration of molybdenum in the organic solution was determined from a mass balance using the concentration of molybdenum in the aqueous solution. The activity of hydrogen ion in the aqueous solution before and after equilibration was determined by a Hitachi-Horiba F-7ss pH meter or neutralization titration.

2. Results

To clarify the characteristics of extraction equilibrium of molybdenum with PC-88A diluted in n-heptane, the effects of pH and concentrations of molybdenum in aqueous solution and of PC-88A in organic solution on the distribution ratio of molybdenum between the organic and aqueous solutions, D_{Mo}, were observed. D_{Mo} is expressed as

$$D_{Mo} = [Mo]_{org}/[Mo]_{aq}$$

where $[Mo]_{org}$ and $[Mo]_{aq}$ are the concentrations of molybdenum in the organic and aqueous solutions in equilibrium.

The effect of pH on D_{Mo} is shown in **Fig. 1**. D_{Mo} increases with pH in the low pH range, but decreases with pH in the high pH range, showing a maximum value around pH = 2. These results are similar to those obtained by Zelikman et al. using D2EHPA in kerosene.[21] In the range of low pH (pH < 0.8), each curve approaches the line of slope nearly equal to 2.

Figures 2, **3** and **4** show the effects of the concentration of extractant on D_{Mo} in the range of low pH. Under the experimental conditions, PC-88A exists mostly as dimer in n-heptane, as shown in the previous paper in which the dimerization constant was determined as $K_D = 3.0$ [m^3/mol].[12]

For each acid solution, in the range of high concentration of PC-88A, the product of D_{Mo} and the square of hydrogen ion activity, $D_{Mo}a_H^2$, is proportional to the square of the dimer concentration of PC-88A, $C_{(HR)_2}$. For sulfuric acid solution, in the range of low concentration of PC-88A, $D_{Mo}a_H^2$ is nearly proportional to the dimer concentration of PC-88A.

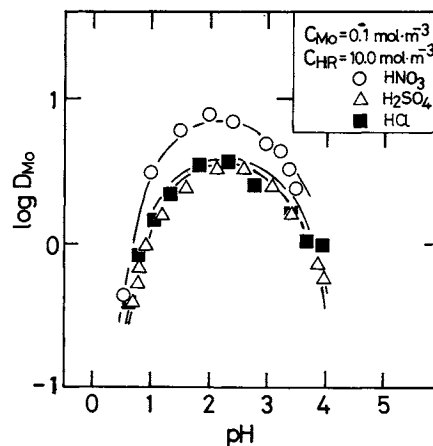## 3. Discussion

Concerning the species of molybdate in aqueous

Fig. 1. Effect of pH on distribution ratio of Mo, D_{Mo} $C_{Mo} = 0.1$ mol/m^3; $C_{(HR)_2} = 10.0$ mol/m^3.
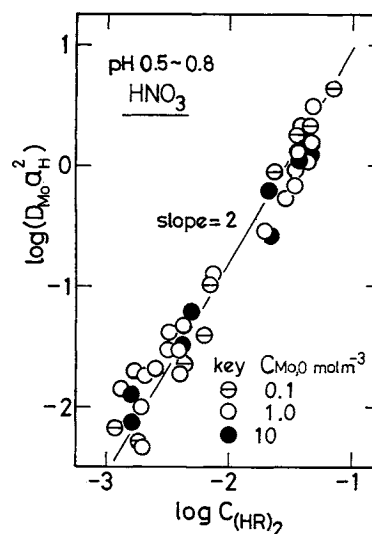

Fig. 2. Effect of extractant concentration on distribution ratio of molybdenum 1000 mol/m^3 (nitric acid-sodium hydroxide aqueous solution).
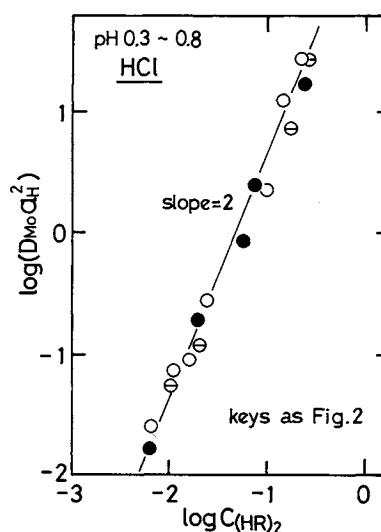

Fig. 3. Effect of extractant concentration on distribution ratio of molybdenum 1000 mol/m^3 (hydrochloric acid-sodium hydroxide aqueous solution).
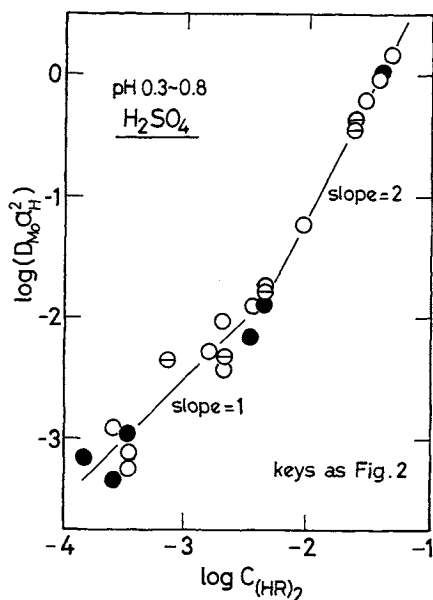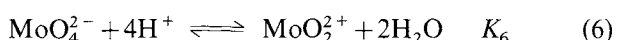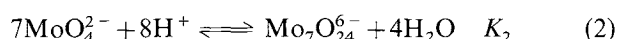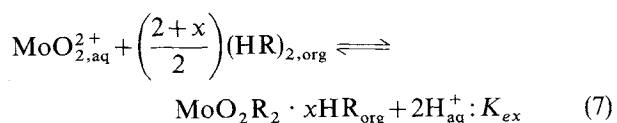
Fig. 4. Effect of extractant concentration on distribution ratio of molybdenum 500 mol/m³ sulfuric acid-1000 mol/m³ sodium hydroxide aqueous solution.

solution, it is well known that molybdate ion in basic aqueous solution exists in the form of MoO_4^{2-} and that a series of molybdenum species, e.q., $Mo_7O_{24}^{6-}$, $HMo_7O_{24}^{5-}$, $H_2Mo_7O_{24}^{4-}$, $HMoO_4^-$, H_2MoO_4 and MoO_2^{2+} increase in the above order as the acidity of aqueous solution increases. In the range of pH <4, the following equilibria of molybdate ions in aqueous solution are considered:

$$MoO_4^{2-} + H^+ \rightleftharpoons HMoO_4^- \qquad K_1 \qquad (1)$$

$$7MoO_4^{2-} + 8H^+ \rightleftharpoons Mo_7O_{24}^{6-} + 4H_2O \quad K_2 \qquad (2)$$

$$Mo_7O_{24}^{6-} + H^+ \rightleftharpoons HMo_7O_{24}^{5-} \qquad K_3 \qquad (3)$$

$$HMo_7O_{24}^{5-} + H^+ \rightleftharpoons H_2Mo_7O_{24}^{4-} \qquad K_4 \qquad (4)$$

$$MoO_4^{2-} + 2H^+ \rightleftharpoons H_2MoO_4 \qquad K_5 \qquad (5)$$

$$MoO_4^{2-} + 4H^+ \rightleftharpoons MoO_2^{2+} + 2H_2O \quad K_6 \qquad (6)$$

The value of each equilibrium constant, except for K_6, was available in the literature as shown in **Table 1**. The cationic species, MoO_2^{2+}, which exists only at a low pH, is extracted by the cation exchange extractant, PC-88A, as follows:

$$MoO_{2,aq}^{2+} + \left(\frac{2+x}{2}\right)(HR)_{2,org} \rightleftharpoons$$

$$MoO_2R_2 \cdot xHR_{org} + 2H_{aq}^+ : K_{ex} \qquad (7)$$

where HR and $(HR)_2$ denote monomer and dimer of PC-88A, respectively, and K_{ex} is the extraction equilibrium constant.

Assuming that only the species $MoO_2R_2 \cdot xHR$ exists in the organic solution, and combining the equilibrium relations shown by Eqs. (1) to (7), $[Mo]_{org}$

Table 1. Equilibrium constants

	Value	
K_1	1.24×10^1	[16]
K_2	5.00×10^{15}	[16]
K_3	2.10×10^1	[16]
K_4	5.00	[16]
K_5	3.98×10^1	[15]
K_6	3.50×10^{-4}	

and $[Mo]_{aq}$ are expressed by the following equations:

$$[Mo]_{org} = K_{ex}[MoO_2^{2+}]\{C_{(HR)_2}\}^{(2+x)/2}/a_H^2 \qquad (8)$$

$$[Mo]_{aq} = [MoO_2^{2+}]\{1 + \alpha_H + \beta_H[MoO_2^{2+}]^6\} \qquad (9)$$

where

$$\alpha_H = K_5/(K_6 a_H^2)(1/(K_5 a_H^2)$$
$$+ K_1/(K_5 a_H) + 1) \qquad (10)$$

$$\beta_H = 7K_2 K_3 K_4/(K_6^7 a_H^{18})(1/(K_3 K_4 a_H^2)$$
$$+ 1/(K_4 a_H) + 1) \qquad (11)$$

$[MoO_2^{2+}]$ is the concentration of MoO_2^{2+} and a_H is the activity of hydrogen ion.

The distribution ratio of molybdenum is obtained from Eqs. (8) and (9), as follows:

$$\log D_{Mo} = \log K_{ex} + 2\log\frac{1}{a_H} + \frac{2+x}{2}\log C_{(HR)_2} - \log Q \qquad (12)$$

where

$$Q = 1 + \alpha_H + \beta_H[MoO_2^{2+}]^6 \qquad (13)$$

By solving Eq. (9) numerically, $[MoO_2^{2+}]^6$ is expressed as a function of $[Mo]_{aq}$ and a_H; that is, Q depends on $[Mo]_{aq}$ and a_H. From mass balance with respect to molybdenum, $[Mo]_{aq}$ is expressed as follows:

$$[Mo]_{aq} = \frac{1}{1 + D_{Mo}(V_{org}/V_{aq})}[Mo]_{aq0} \qquad (14)$$

where V_{org} and V_{aq} are the volumes of the organic and aqueous solutions, respectively, and $[Mo]_{aq0}$ is the initial concentration of molybdenum in the aqueous solution. By using Eqs. (9) to (14), the relation between D_{Mo} and the concentration of each species is calculated numerically. In the range of pH <0.8 in Fig. 1, Q is assumed nearly equal to 1.0, because a slope of 2 indicates that the molybdenum species in the aqueous solution exists as MoO_2^{2+}, as anticipated from Eq. (12), and so Eq. (12) is rewritten as follows:

$$\log D_{Mo} a_H^2 = \log K_{ex} + \frac{2+x}{2}\log C_{(HR)_2} \qquad (15)$$

From the experimental results in the range of high concentration of PC-88A, shown in Figs. 2 to 4, x was

found to be 2 and so K_{ex} is obtained as 1.36×10^3, 0.81×10^3 and 0.74×10^3 in nitric acid, hydrochloric acid and sulfuric acid solution, respectively. It is considered that the K_{ex} value is affected by complex formation of molybdenum with each anionic species in aqueous solution such as MoO_2Cl_2 and $MoO_2(NO_3)_n^{2-n}$. [13,20]

In the case of sulfuric acid medium, in the range of low concentration of PC-88A the value of x is changed to zero and $K_{ex} = 2.72 \times 10^3 \, mol/m^3$ was obtained. In the range of low concentration of PC-88A in the cases of hydrochloric and nitric acid solutions, it is anticipated that the same tendency for x to change as obtained in sulfuric acid solution can be observed, though it was not confirmed due to limitation for detection of molybdenum by atomic absorption spectrophotometer.

From using the experimental results for each acid solution and Eqs. (9) to (14), the value of K_6 was determined to be $K_6 = 3.50 \times 10^{-4} \, [(mol/m^3)^{-4}]$.

The solid lines in Fig. 1 were calculated from Eqs. (9) to (14) by using the equilibrium constants shown in **Tables 1** and **2**. **Figure 5** shows the relations between the mole fraction of each species and pH, which are obtained from the equilibrium equations (1) to (6), showing that the cationic species MoO_2^{2+} is the predominant species in the range of pH < 0.8, that is, $Q = 1.0$.

Figure 6 shows a comparison between the calculated and observed distribution ratios. Close agreement was obtained.

Conclusion

The extraction equilibrium of molybdenum(VI) from nitric, hydrochloric and sulfuric acid aqueous solutions with PC-88A in n-heptane was examined at 303 K. The extraction equilibrium constant, K_{ex}, was obtained for each acid solution, and the K_{ex} value became greater in the order $HNO_3 > HCl > H_2SO_4$.

The effect of pH on the distribution ratio of molybdenum, D_{Mo}, was interpreted by taking account of the equilibrium concentration of a cationic species of molybdenum in the aqueous solution. From all experimental results, the value of K_6 was obtained by the nonlinear least square method.

Nomenclature

a_H	= activity of hydrogen ion	$[mol/m^3]$
$C_{(HR)_2}$	= dimer concentration of PC-88A	$[mol/m^3]$
D_{Mo}	= distribution ratio	[—]
K_{ex}	= extraction equilibrium constant	[—]
K_1	= equilibrium constant defined by Eq. (1)	$[(mol/m^3)^{-1}]$
K_2	= equilibrium constant defined by Eq. (2)	$[(mol/m^3)^{-14}]$
K_3	= equilibrium constant defined by Eq. (3)	$[(mol/m^3)^{-1}]$

Table 2. Extraction equilibrium constants

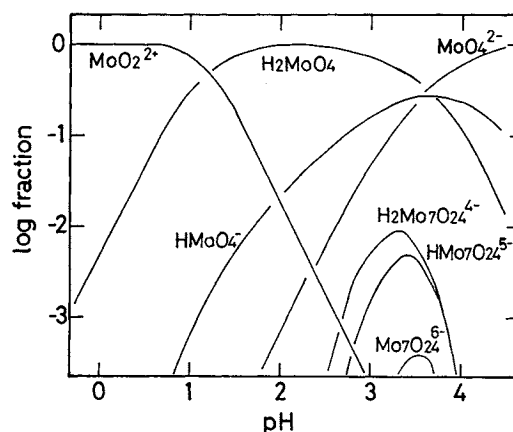|			
HNO_3	1.36×10^3	[—]	
HCl	0.81×10^3	[—]	
H_2SO_4	0.74×10^3	[—]	in high $C_{(HR)_2}$
	2.72×10^3	$[mol/m^3]$	in low $C_{(HR)_2}$

Fig. 5. Profile of abundance (log fraction) of each Mo(VI) species along the pH range ($C_{Mo} = 0.1 \, mol/m^3$).
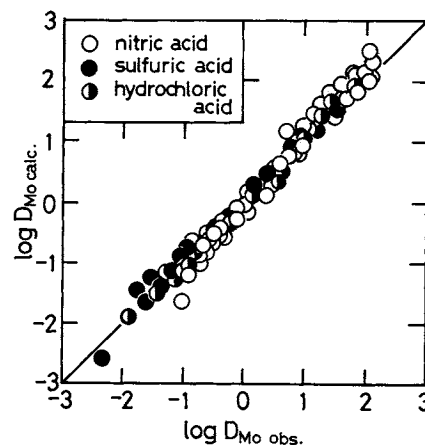

Fig. 6. Comparison of experimental results with calculated results of distribution ratio.

K_4	= equilibrium constant defined by Eq. (4)	$[(mol/m^3)^{-1}]$
K_5	= equilibrium constant defined by Eq. (5)	$[(mol/m^3)^{-2}]$
K_6	= equilibrium constant defined by Eq. (6)	$[(mol/m^3)^{-4}]$
Q	= constant defined by Eq. (13)	[—]
V_j	= volume (j = aq, org)	$[m^3]$
x	= number of additional molecules of extractant in extracted species	[—]
α_H	= constant defined by Eq. (10)	[—]
β_H	= constant defined by Eq. (11)	$[(mol/m^3)^{-6}]$
[ ]	= concentration	$[mol/m^3]$

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SPECIFIC GAS-LIQUID INTERFACIAL AREA AND LIQUID-PHASE MASS TRANSFER COEFFICIENT IN A SLURRY BUBBLE COLUMN

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Introduction

Slurry bubble columns have been widely applied to such industrial processes as coal liquefaction, Fischer-Tropsch synthesis, biological waste water treatment and fermentation. In these processes, the rate of gas-liquid mass transfer, which is characterized by the volumetric mass transfer coefficient $k_l a$, may be controlling to the overall rate. To explain further the gas-liquid mass transfer phenomena in a slurry bubble column, it is very important to study the behavior of k_l, the liquid-phase mass transfer coefficient, and a, the specific gas-liquid interfacial area, independently. Little information, however, is available about a and k_l in a slurry bubble column.

From the experimental data on $k_l a$, gas holdup and volume-surface mean bubble diameter in our previous works[3,15,16] the values of a and k_l in a slurry bubble column were separately evaluated and their behavior

was investigated and correlated in the present paper.

1. Specific Gas-Liquid Interfacial Area, a

The value of a can be evaluated from the mean (or cross-sectionally averaged) gas holdup, $\bar{\varepsilon}_g$, and the volume-surface mean bubble diameter, d_{vs}, as follows.

$$a = 6\bar{\varepsilon}_g / d_{vs} \qquad (1)$$

Our previous study[16] showed that the data on $\bar{\varepsilon}_g$ were expressed by the correlation of Koide *et al.*[7] for heterogeneous flow in the range where the mean solid holdup, $\bar{\varepsilon}_s$, was less than 0.4. It was also shown that the data on d_{vs} was expressed well by the following equation.[3]

$$d_{vs} = 0.59(V_D/\bar{\varepsilon}_g)^2/g \qquad (2)$$

where g is the gravitational acceleration and V_D is the drift flux of gas defined as follows.[14]

$$V_D = U_g(1 - \bar{\varepsilon}_g) - U_l \bar{\varepsilon}_g(1 - \bar{\varepsilon}_g)/\bar{\varepsilon}_l \qquad (3)$$

Figures **1** and **2** show the variation of a evaluated