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Separation of Molybdenum(VI) and Tungsten(VI) through a Supported Liquid Membrane Impregnated with Trioctylmethylammonium Chloride

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ABSTRACT

Transport separation of molybdenum(VI) through a supported liquid membrane (SLM) was investigated by employing trioctylmethylammonium chloride (TOMAC) as a mobile carrier. The transport behavior of Mo(VI) and W(VI) was greatly dependent on hydrochloric acid and chloride ion concentrations in the feed solution. Molybdenum(VI) was effectively transported together with W(VI) from dilute HCl solutions in the presence of 0.1 M tartaric acid into NaOH stripping solutions. Molybdenum(VI) in high HCl concentration was transported in preference to W(VI). Addition of NaCl to the feed solution reduced the W(VI) transport, and this enhanced the separation of Mo(VI) from W(VI). Lower TOMAC concentration in SLM was favorable for the separation of the two metal ions, and a separation factor ($\alpha_{Mo/W}$) of 46 was obtained with 0.1 M TOMAC-SLM.

INTRODUCTION

Molybdenum is usually accompanied by tungsten in the hydrometallurgical processing of tungsten ore. The separation of these metal ions by conventional processes usually requires tedious techniques (1). We have previously investigated the recovery and separation of these metals with a chelating polymer resin and a chelating extractant (2, 3). These metals in aqueous solutions are present in several forms of oxo-anionic species having similar chemical properties (4–7). However, cationic Mo(VI) species are predominant in strongly acidic solutions while cationic W(VI) species rarely exist (8).

The extraction of these metals with trioctylmethylammonium chloride (TOMAC) was known to proceed through anion-exchange reactions. In relatively high concentration of hydrochloric acid, Mo(VI) forms anionic chloro complexes (9) which are considered to be highly extractable with TOMAC in comparison with W(VI) species.

The application of liquid–liquid extraction of these metal ions to liquid membrane transport appears to be an important subject. In the preceding study, Mo(VI) was effectively transported across a supported liquid membrane (SLM) impregnated with TOMAC (10).

In the present study, the extraction behavior of Mo(VI) and W(VI) with TOMAC in kerosene has been examined, and the utility of a liquid membrane impregnated with TOMAC has been proposed for the recovery and separation of these metals.

EXPERIMENTAL

Materials

Trioctylmethylammonium chloride (Koei Chemical Ind. Co.) was diluted with kerosene and modified with 10% (v/v) 1-octanol unless otherwise noted. Aqueous solutions of Mo(VI) and W(VI) were prepared by respectively dissolving Na_2MoO_4 and Na_2WO_4 (Wako Pure Chemical Ind.) in water. Tartaric acid (Wako Pure Chemical Ind.) was added to the acidic solution of W(VI) to prevent its precipitation. A polytetrafluoroethylene membrane (FP-045; Sumitomo Electric Ind.) with a thickness of 80 μm, a porosity of 74%, and an average pore size of 0.45 μm was used as an inert support. Other reagents were of guaranteed grade.

Extraction Equilibrium

An aqueous solution (10 cm^3) containing 5×10^{-4} M (M = $mol \cdot dm^{-3}$) each Mo(VI) and W(VI) was shaken with an equal volume of the kerosene solution of TOMAC for 15 minutes at 25°C. After phase separation by centrifugation, the concentrations of metal ions in the aqueous phase were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) with a Seiko SPS 1200A spectrometer at 202.030 and 224.875 nm for Mo(VI) and W(VI), respectively. The metal concentration in the organic phase was calculated from the differences in concentrations between the aqueous phase before and after extraction.

Liquid Membrane Transport

Transport experiments through the SLM were carried out using an apparatus comprised of inner and outer polypropylene compartments (11). The membrane (26 cm^2) was attached to the bottom of the inner compartment and impregnated with a kerosene solution of TOMAC and 1-octanol. A feed solution (100 cm^3) containing metal ions was placed in the outer compartment, and an equal volume of the product solution was placed in the inner compartment. The apparatus was horizontally shaken at 120 strokes/min at 25°C. Samples were taken from the feed and product solutions at time intervals and analyzed for metal concentrations by ICP-AES.

RESULTS AND DISCUSSION

Liquid–Liquid Extraction

Molybdenum(VI) and tungsten(VI) are present in the form of MoO_4^{2-} and WO_4^{2-}, respectively, in alkaline aqueous solutions and are extractable with TOMAC through anion-exchange reactions by the following equations (12):

$$R_3R'NCl_{(o)} + OH^- \rightleftarrows R_3R'NOH_{(o)} + Cl^- \qquad (1)$$

$$MO_4^{2-} + 2R_3R'NOH_{(o)} \rightleftarrows (R_3R'N)_2MO_{4(o)} + 2OH^- \qquad (2)$$

where M represents Mo or W, $R_3R'NCl$ represents TOMAC, and the subscript "(o)" refers to the organic phase. Extraction behavior of the two metals was investigated at different concentrations of NaOH by using 0.1 M TOMAC and 10% 1-octanol in kerosene. Figure 1 shows the logarithmic plot of the distribution ratios (*D*) of Mo(VI) and W(VI) against NaOH concentration. The *D* values were high at low NaOH concentration and decreased with increasing NaOH concentration. The extraction of the two metal species proceeded in a similar manner, and their separation may be difficult under these conditions.

In a strong acidic region, Mo(VI) differs from W(VI) in chemical species. Figure 2 illustrates the extraction behavior of metal ions in a wide concentration region of HCl. Here, the solubility of W(VI) in mineral acids is generally low, and hence 0.1 M tartaric acid was present to prevent precipitation. The distribution ratio of Mo(VI) decreased with increasing HCl concentration, lowered down to a minimum at about 1.5 M, and then sharply increased at higher acid concentrations. The extraction of W(VI) also decreased along with increasing HCl concentration and then slightly increased above 2 M HCl.

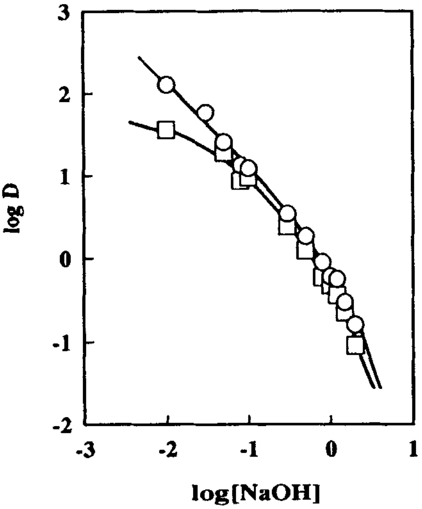

FIG. 1 Extraction of Mo(VI) and W(VI) from NaOH solution with 0.1 M TOMAC and 10% 1-octanol in kerosene. (○) Mo, (□) W.

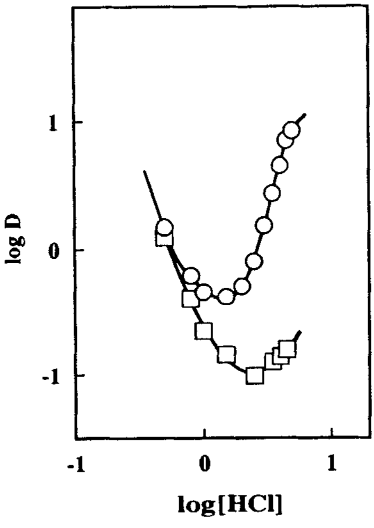

FIG. 2 Extraction of Mo(VI) and W(VI) from HCl solution in the presence of 0.1 M tartaric acid with 0.1 M TOMAC and 10% 1-octanol in kerosene. (○) Mo, (□) W.

It is deduced from the above results that the metal extraction proceeds by the formation of different metal species at low and high concentration regions of HCl. Molybdenum (VI) forms extractable anionic complexes with tartaric acid at low HCl concentration (13, 14). The formation of these anionic species was reduced at high HCl concentration owing to depression of dissociation of tartaric acid. At higher HCl concentration (above 1.5 M), the distribution ratio sharply increased due to the formation of anionic chloro complexes. Selmer-Olsen has reported a similar comment (15). The extraction of W(VI) from a low acidic region proceeded in a similar manner to the Mo(VI) case owing to the formation of corresponding tartarate anionic complexes (16). As the HCl concentration increased, the *D* values of W(VI) remained in the lower level because of the smaller tendency for the formation of extractable W(VI)–chloro complexes (17). Preferential extraction of anionic chloro species of Mo(VI) would provide a promising separation process.

The addition of long-chain alcohol to the kerosene solution of TOMAC served to enhance the solubilities of the reagent and its complex in the organic phase (18). The effect of 1-octanol content in the organic phase on the *D* values of Mo(VI) and W(VI) was tested. As Fig. 3 shows, the metal extraction decreased with increasing 1-octanol content up to 20% and was unchanged at higher concentration. The decrease in extraction may be due to the interaction of 1-octanol with TOMAC (19).

The effect of TOMAC concentration in the presence of 10% 1-octanol on the *D* values is illustrated in Fig. 4. Logarithmic plots of *D* against the

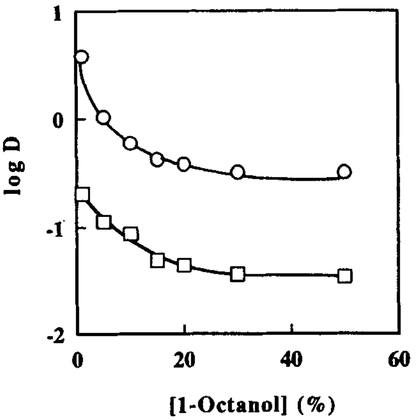

FIG. 3 Effect of 1-octanol concentration on extraction of Mo(VI) and W(VI) from 3 M HCl in the presence of 0.1 M tartaric acid. Organic phase: 0.05 M TOMAC and 1-octanol in kerosene. (○) Mo, (□) W.

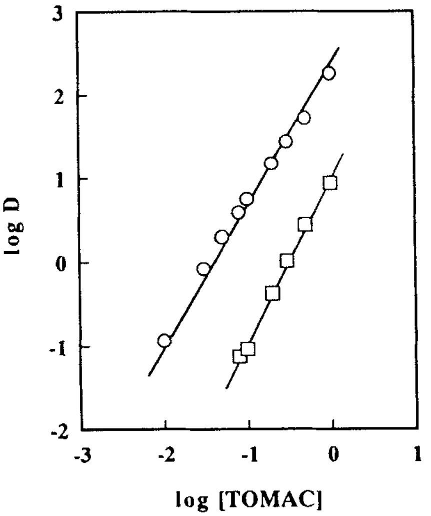

FIG. 4 Effect of TOMAC concentration on extraction of Mo(VI) and W(VI). Organic phase: TOMAC and 10% 1-octanol in kerosene. Aqueous phase: 4 M HCl and 0.1 M tartaric acid. (○) Mo, (□) W.

TOMAC concentration gave straight lines with slopes near 2, indicating the participation of two molecules of TOMAC in the extracted complexes. The extraction of Mo(VI) was higher than that of W(VI).

Application to the SLM Transport

TOMAC was verified to be an effective extractant of Mo(VI) and W(VI), and it could be utilized as a mobile carrier in SLM transport of these metals. The addition of 10% 1-octanol in the kerosene solution of TOMAC was found to stabilize the membrane, and it was employed in the following experiments. The extraction from concentrated NaOH solutions was very poor, and this appears to be suitable for stripping.

Figure 5 illustrates the transport of Mo(VI) and W(VI) through SLM impregnated with 1 M TOMAC from a 0.1 M HCl solution in the presence of 0.1 M tartaric acid into a 1 M NaOH stripping solution. The two metal ions were almost completely removed from the feed solution after about 3 hours, and more than 97% of Mo(VI) and 91% of W(VI) were recovered into the product side after transport performance for 7 hours. These metal ions are considered to be extracted as tartarate species from the dilute HCl feed solution into the SLM phase and then released into the NaOH product solution.

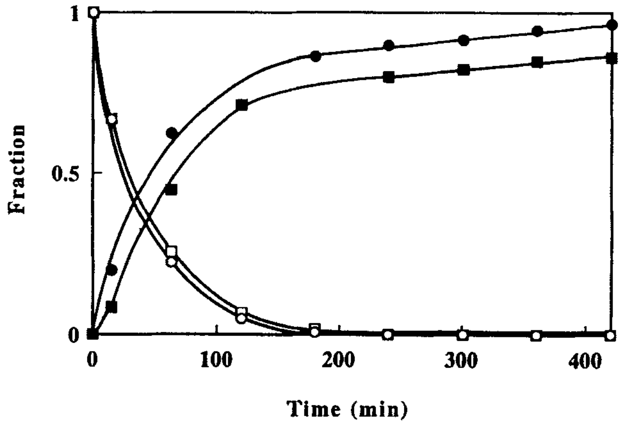

FIG. 5 Transport of Mo(VI) and W(VI) from 0.1 M HCl into 1 M NaOH through SLM containing 1 M TOMAC and 10% 1-octanol in kerosene. (○, ●) Mo, (□, ■) W. Open symbol: feed. Filled symbol: product.

The transport behavior of Mo(VI) is similar to that of W(VI) at low acidity, and the two metals are inseparable. As was emphasized in Fig. 2, higher HCl concentration looks promising for preferential·extraction of Mo(VI) and for depressing extraction of W(VI). The time-dependent fractions of Mo(VI) and W(VI) across the membrane from 4 M HCl are represented in Fig. 6. The fraction of Mo(VI) in the feed solution decreased with shaking time, and that in the product solution increased nearly symmetrically. Mo(VI) was nearly quantitatively transported after 7 hours as well as being transported at low acidity. The transport of W(VI) was considerably low in comparison with the transport from dilute HCl solution. Thus, the transport from high HCl concentration was desirable for preferential transport of Mo(VI).

The decreasing rate of the metal ion in the feed solution is expressed by

$$\ln([\mathrm{M}]_{\mathrm{f,t}}/[\mathrm{M}]_{\mathrm{f,o}}) = -k_{\mathrm{f,obs}}t$$

where $[\mathrm{M}]_{\mathrm{f,t}}$ and $[\mathrm{M}]_{\mathrm{f,0}}$ denote the concentrations of the metal ion at times t and zero in the feed solution, respectively, and $k_{\mathrm{f,obs}}$ (s^{-1}) is the apparent rate constant.

The transport parameters obtained at different HCl concentrations in the feed solution are summarized in Table 1. The $k_{\mathrm{f,obs}}$ value of Mo(VI) decreased along with an increase in HCl concentration below 1 M and then slightly increased at higher concentration, reflecting a similar trend

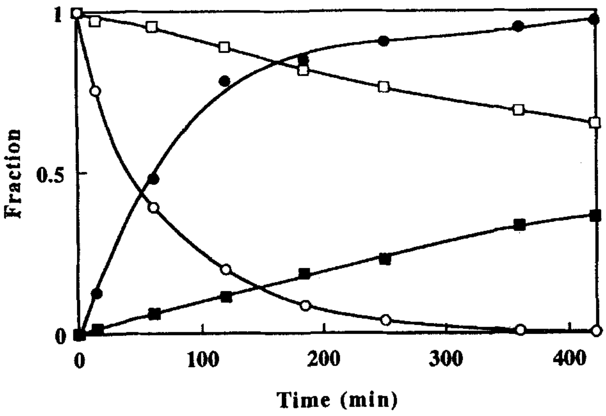

FIG. 6 Transport of Mo(VI) and W(VI) from 4 M HCl. Other conditions are the same as in Fig. 5. (○, ●) Mo, (□, ■) W. Open symbol: feed. Filled symbol: product.

observed in liquid–liquid extraction. On the other hand, the $k_{f,obs}$ value for W(VI) decreased with increasing HCl concentration up to 4 M.

The separation factor ($\alpha_{Mo/W}$), defined as the ratio of the $k_{f,obs}$ values for Mo(VI) and W(VI), was enhanced at high HCl concentration and reached 12 at 4 M HCl.

Effect of Acidity and Chloride Ion Concentration

The extraction of these metal ions with TOMAC is controlled by the aqueous acidity and the chloride ion concentration (10, 20, 21). In order

TABLE 1
Effect of HCl Concentration in Feed Solution on Transport of Mo(VI) and W(VI)[a]

[HCl] (M)	$10^5 \cdot k_{f,obs}$ (s^{-1})		$\alpha_{Mo/W}$[b]	Recovery (%), 7 hours	
	Mo	W		Mo	W
0.1	28.2	21.5	1.3	97.1	91.8
0.5	21.0	12.9	1.6	95.0	89.5
1.0	10.8	5.4	2.0	88.9	67.9
2.0	11.2	3.3	3.4	96.5	52.4
3.0	14.4	1.8	8.0	97.7	38.7
4.0	19.8	1.7	12	97.9	36.1

[a] SLM: 1 M TOMAC and 10% 1-octanol in kerosene. Product: 1 M NaOH.

[b] Separation factor, $\alpha_{Mo/W} = k_{f,obs}(Mo)/k_{f,obs}(W)$.

to accomplish the separation of Mo(VI) from W(VI), conditions of the feed solution should be optimized to enhance Mo(VI) transport and to suppress W(VI) transport. The experimental results given in Table 1 may be affected by variations in acidity and chloride ion concentration.

The effect of differences in acidity on the transport of Mo(VI) and W(VI) was tested on keeping the total concentration of chloride ion at 4 M by the addition of NaCl. The experimental results are presented in Table 2. At low acidity the transport of Mo(VI) was rather suppressed, and the $k_{f,obs}$ value for Mo(VI) transport increased along with acid concentration. As for W(VI), the $k_{f,obs}$ value remained practically unchanged irrespective of HCl concentration below 2 M and slightly increased at higher acidity. The $\alpha_{Mo/W}$ values were found to be around 12 at HCl concentration above 0.5 M; however, these are still low for mutual separation.

In order to enhance the separation of Mo(VI) from W(VI), it will be required to reduce the transport of W(VI). Transport data obtained by varying the chloride ion concentration on keeping the HCl concentration at 1 M are summarized in Table 3. The $k_{f,obs}$ value for Mo(VI) transport remained at relatively higher level in a wide concentration region of Cl^-, whereas that for W(VI) transport sharply decreased along with an increase in chloride ion concentration. The W(VI) transport was thus further depressed at higher concentration of chloride ion, and this improved the separation of Mo(VI) from W(VI). The separation factor was enhanced to be 21 at 1 M HCl–4 M NaCl in the feed solution. About 97% of Mo(VI) was recovered together with about 16% of W(VI) after 7 hours under these conditions.

Effect of Stripping NaOH Concentration

Effects of NaOH concentration in the product solution on the metal transport are summarized in Table 4. The concentration of NaOH had

TABLE 2

Effect of Acidity at 4 M (H,Na)Cl in Feed Solution on Transport of Mo(VI) and W(VI)[a]

[HCl] (M)	[NaCl] (M)	$10^5 \cdot k_{f,obs}$ (s^{-1}) Mo	W	$\alpha_{Mo/W}$	Recovery (%), 7 hours Mo	W
0.1	3.9	3.9	1.0	3.9	59.7	18.0
0.5	3.5	9.8	0.9	11	90.8	17.9
1.0	3.0	12.3	0.9	14	96.1	18.6
2.0	2.0	16.2	1.5	11	97.5	24.5
4.0	0.0	19.8	1.7	12	97.9	36.1

[a] SLM: 1 M TOMAC and 10% 1-octanol in kerosene. Product: 1 M NaOH.

TABLE 3

Effect of Chloride Ion Concentration at 1 M HCl in Feed Solution on Transport of Mo(VI) and W(VI)[a]

[HCl] (M)	[NaCl] (M)	$10^5 \cdot k_{f,obs}$ (s^{-1})			Recovery (%), 7 hours	
		Mo	W	$\alpha_{Mo/W}$	Mo	W
1.0	0.0	10.8	5.4	2.0	88.9	67.9
1.0	0.5	10.2	3.4	3.0	87.1	51.9
1.0	1.0	9.7	2.3	4.2	81.6	37.2
1.0	2.0	10.2	1.3	7.8	86.3	22.9
1.0	3.0	12.3	0.9	14	96.1	18.6
1.0	4.0	14.7	0.7	21	96.9	16.4
1.0	Sat.[b]	15.7	0.7	22	97.5	16.7

[a] SLM: 1 M TOMAC and 10% 1-octanol in kerosene. Product: 1 M NaOH.

[b] Saturated NaCl solution.

little effect on the $k_{f,obs}$ value as long as the stripping ability was sufficiently high. The recovery of Mo(VI) was poor into the dilute NaOH solutions and became almost quantitative at a NaOH concentration higher than 1 M. The recovery of W(VI) also increased with NaOH concentration.

Effect of TOMAC Concentration

Transport parameters related to variation in TOMAC concentration are listed in Table 5. The $k_{f,obs}$ value for Mo(VI) transport slightly increased

TABLE 4

Effect of NaOH Concentration in Product Solution on Transport of Mo(VI) and W(VI)[a]

[NaOH] (M)	$10^5 \cdot k_{f,obs}$ (s^{-1})			Recovery (%), 7 hours	
	Mo	W	$\alpha_{Mo/W}$	Mo	W
0.1	20.1	1.6	13	15.4	0.2
0.5	21.4	1.6	13	22.7	7.3
1.0	19.8	1.7	12	97.9	36.1
1.5	21.9	1.6	14	98.8	36.5
2.0	23.8	1.8	13	99.0	36.7

[a] Feed: 4 M HCl. SLM: 1 M TOMAC and 10% 1-octanol in kerosene.

TABLE 5
Effect of TOMAC Concentration on Transport of Mo(VI) and W(VI)[a]

[TOMAC] (M)	$10^5 \cdot k_{f,obs}$ (s^{-1})		$\alpha_{Mo/W}$	Recovery (%), 7 hours	
	Mo	W		Mo	W
0.05	4.9	0.08	61	45.2	0.9
0.10	5.1	0.11	46	75.1	2.8
0.50	10.7	0.34	31	88.9	8.5
0.75	13.6	0.53	26	93.0	12.8
1.00	14.7	0.73	20	96.3	16.4

[a] Feed: 1 M HCl and 4 M NaCl. SLM: TOMAC in the presence of 10% 1-octanol in kerosene. Product: 1 M NaOH.

with TOMAC concentration in the tested region from 0.05 to 1 M. The values for W(VI) transport were at a lower level and progressively increased with TOMAC concentration. The $\alpha_{Mo/W}$ value therefore became lower at higher TOMAC concentration. Though the Mo(VI) transport was suppressed to some extent at lower concentration of TOMAC, it is important to reduce the W(VI) transport in order to enhance the $\alpha_{Mo/W}$ value, e.g., 46 with 0.1 M TOMAC. The transport test with 0.1 M TOMAC gave

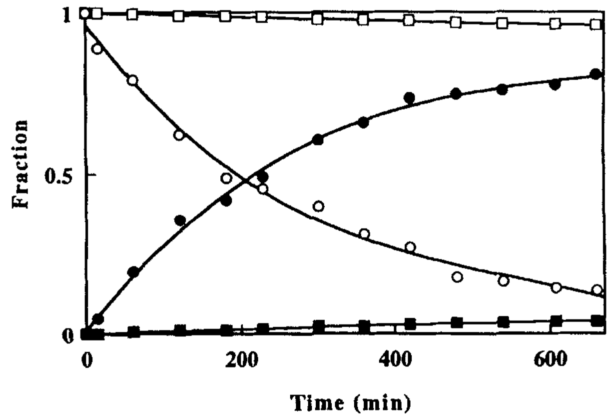

FIG. 7 Transport of Mo(VI) and W(VI) from 1 M HCl and 4 M NaCl through 0.1 M TOMAC and 10% 1-octanol into 1 M NaOH. (○, ●) Mo, (□, ■) W. Open symbol: feed. Filled symbol: product.

reasonable separation of Mo(VI) and W(VI), that is, 75% of Mo(VI) was recovered after 7 hours together with only 2.8% of W(VI). When the transport time was prolonged, e.g., to 11 hours, more than 80% of Mo(VI) was also recovered along with 3.7% of W(VI) in the product solution, as illustrates in Fig. 7. Further increase in TOMAC concentration in SLM increased the recovery not only of Mo(VI) but also of W(VI) into the product side, and then the separation became rather unsatisfactory.

The transport separation of Mo(VI) was thus accomplished across a SLM containing a low concentration of TOMAC at a higher concentration of chloride ion.

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