EXTRACTION AND SEPARATION OF MOLYBDENUM AND VANADIUM USING BIS(2-ETHYLHEXYL)MONOTHIOPHOSPHORIC ACID AND BIS(2-ETHYLHEXYL)PHOSPHORIC ACID

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The extraction of molybdenum and vanadium from weak-acidic sulfate and chloride media by bis (2-ethylhexyl)monothiophosphonic acid (D2EHTPA) and bis (2-ethylhexyl) phosphoric acid (D2EHPA) was investigated. The cationic species of the metals, such as MoO42-, were extracted by both extractants. In the case of vanadium, the supplied VO4 was reduced to VO2+ by contact with the organic phase containing D2EHTPA, and this extractant was partially oxidized to disulfide. While molybdenum was found to be more extractable than vanadium by both extractants, the separation factor of the metals by using D2EHTPA was greater than in the case using D2EHPA, especially when VO4 was used as feed. The oxidized D2EHTPA containing disulfide enhanced the extractability of molybdenum and vanadium. However, the separation factor of the metals decreased with the formation of disulfide. It is important to reduce V(V) to VO2+ prior to extraction in order to minimize the oxidation of D2EHTPA for separation and repeated use of the extractant.

Introduction

The molybdate and vanadate ions form various types of uni- and multi-nuclear oxo-complexes in aqueous solution depending on solution pH and concentration of the ions. Thus, for the separation and purification of two metals by solvent extraction, an appropriate extractant must be selected to extract and separate these ions under aqueous-phase conditions. It has been reported that these metals can be separated from hydrochloric acid solution by using tri-n-butyl phosphate (TBP), from sulfuric acid solution by bis (2-ethylhexyl) phosphoric acid (D2EHPA) and from sulfite solution by tri-n-octylamine (TOA) at pH 2.5. Separation of the metals by extraction using tri-n-octylmethylammonium chloride (TOMAC) from neutral solution followed by reductive stripping of vanadium was also investigated.

Molybdenum and vanadium are contained in spent desulfurizing catalyst and also in oil-fired boiler slag. In a previous work, recovery of nickel, molybdenum and vanadium from spent desulfurizing catalyst was investigated. There, the three elements were successively isolated from a leach liquor using a single extractant, bis(2-ethylhexyl)monothiophosphoric acid (D2EHTPA), employing a suitable pH value for each metal. The extraction equilibrium for nickel with D2EHTPA was found to be identical to that established with D2EHPA.

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However, the extraction behavior of molybdenum and vanadium was varied, depending on the feed concentration of the metal and pH value. This might arise from variation of the ionic species in the aqueous solution.

In this work, the extraction and separation of molybdenum and vanadium by D2EHTPA and D2EHPA have been investigated. Extraction equilibria for molybdenum and vanadium have been formulated. D2EHPA is an established extractant and known to be resistant to oxidation. D2EHTPA is, however, unlikely to be resistant to oxidation, since it contains thiol groups. In addition, pentavalent vanadium has been found to be reduced to tetra or trivalent vanadium by electrochemical and photochemical methods. Possible oxidation and reduction of the extractant and the metal ions encountered in the extraction have been investigated and the resultant effect on the extraction of the two metals has also been investigated.

1. Experimental

1.1 Reagents

The commercial extractants, bis (2-ethylhexyl) monothiophosphonic acid (D2EHTPA, commercial name: MSP-8) and bis(2-ethylhexyl) phosphoric acid (D2EHPA, commercial name: DP-8R), were supplied by Daihachi Chemical Ind. Co., Ltd., Osaka, and were purified by the procedure developed for purification of D2EHPA by Partridge and Jensen. Kerosene of industrial grade was used as a diluent. Aquous solutions of molybdenum and vanadium were prepared by dissolving Na2MoO4·2H2O,
NaVO₃ or VOSO₄·nH₂O, respectively, in H₂SO₄-Na₂SO₄, H₂SO₄-(NH₄)₂SO₄ or HCl-NaCl solution. The salt concentrations of these solutions were adjusted to required values with Na₂SO₄, (NH₄)₂SO₄ and NaCl. All inorganic chemicals were supplied by Wako Pure Chemical Ind. Ltd. as analytically pure reagent grade.

1.2 Procedures

Extraction of the metals was carried out by shaking organic and aqueous feed solutions, with volume ratio 1 : 1, for 3 h in a thermostat bath at 298 K to allow time for equilibrator. After the two phases had been allowed to settle for 3 h, they were separated. Metal-loaded organic solutions were completely stripped with 3 M NaOH for molybdenum and with 1 M HCl for vanadium (M = mol/dm³). The resulting aqueous samples were analyzed for metal using an inductively coupled argon plasma emission spectrophotometer (ICP, Nippon Jarrell-Ash ICAP-575 Mark II). Visible absorption spectra of aqueous and organic solutions containing metal ions or metal complexes were obtained using a Shimadzu UV-265FW spectrophotometer.

2. Results and Discussion

2.1 Extraction of molybdenum

Molybdenum species in aqueous solutions form uni- or multi-nuclear oxo-complexes. The mole fractions of the molybdenum species can be calculated as a function of solution pH according to the following equilibrium equations, assuming that no multi-nuclear species is formed at the low molybdenum concentrations employed in the present work.

\[
\text{MoO}_4^{2-} + H^+ = H\text{MoO}_4^- \quad K_1 = 10^{4.08} \tag{1}
\]

\[
\text{MoO}_4^{2-} + 2H^+ = H_2\text{MoO}_4 \quad K_2 = 10^{7.75} \tag{2}
\]

Fig. 1. Effect of pH on distribution ratio of MoO₄²⁻ in (a) sulfate and (b) chloride systems

Fig. 2. Effect of concentration of extractant on distribution ratio of MoO₄²⁻

\[
\text{MoO}_4^{2-} + 4H^+ = \text{MoO}_2^{2+} + 2H_2O, \quad K_3 = 10^{9.54} \tag{3}
\]

Actually, there is no significant difference between the mole fraction of the cationic species, MoO₂²⁺, calculated by using the above three equations, and that calculated taking the formation of multi-nuclear species into consideration as well. Both D2EHPA and D2EHPA are considered to extract the cationic species of molybdenum. Two kinds of distribution ratio, D and D’, are thus considered. D is defined by using total concentration of molybdenum species in the aqueous solution and D’ by using concentration of MoO₂²⁺ species. When j-merized extract is formed, the two ratios are expressed as follows.

\[
D = \frac{[\text{Mo}]}{[\text{Mo}]_j} \left[ \text{MoO}_2^{2+} \right] + \left[ \text{HMO}_2^- \right] + \left[ H_2\text{MO}_4 \right] + \left[ \text{MoO}_4^{2-} \right] \tag{4}
\]

\[
D' = \frac{[\text{Mo}]}{[\text{MoO}_2^{2+}]} \tag{5}
\]

A plot of D' against aqueous-phase pH is shown in Fig. 1. A straight line with slope of 2 is obtained both in the sulfate and chloride systems, whereas the plot of D does not give a straight line. The plot of [Mo] × [H⁺]² against [MoO₂²⁺] at constant D2EHPA concentration was found to give a straight line of slope 1, indicating the extracted species is monomeric (j = 1).

D2EHPA was found to be a dimeric form, (LH)₂₂, in non-polar solvents by a vapor-phase osmometric
Table 1. Extraction equilibrium constants for molybdenum

<table>
<thead>
<tr>
<th>Extractant</th>
<th><strong>D2EHPA</strong></th>
<th><strong>K_ex1 [M]</strong></th>
<th><strong>K_ex2 [M]</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>[(Na₂, H)SO₄] = 1M</td>
<td>2.1 x 10⁻ⁱ</td>
<td>1.6</td>
<td>3.1 x 10⁻²</td>
</tr>
<tr>
<td>[(Na, H)Cl] = 1M</td>
<td>4.1 x 10⁻¹</td>
<td>6.1</td>
<td>2.9 x 10⁻¹</td>
</tr>
</tbody>
</table>

Fig. 3. Effect of loading ratios of D2EHPA solution with (a) molybdenum and (b) vanadium on extraction equilibrium constants for sulfate system. VOSO₄ was used as feed in the case of vanadium.

Fig. 4. Effect of pH on distribution ratio of VO²⁺ in (a) sulfate and (b) chloride systems

\[ D'\left[\text{H}^+\right]^2 / \left[\text{[(LH)_2]}\right] = K_{ex1} \left[\text{[(LH)_2]}\right] + K_{ex2} \] (10)

The plot of \( D'\left[\text{H}^+\right]^2 / \left[\text{[(LH)_2]}\right] \) against \( \left[\text{[(LH)_2]}\right] \) gives a straight line, with a slope equal to \( K_{ex1} \) and an intercept equal to \( K_{ex2} \). The extraction equilibrium constants thus obtained are shown in Table 1 for chloride and sulfate systems.

**Figure 3** shows the effect of loading ratio on the extraction equilibrium constant for the sulfate system. The apparent value remains constant up to 0.2. The formulation shown by Eq. (6) may be valid in the range of D2EHPA conversion less than 30%.

In the case of D2EHPA, the extraction equilibrium was formulated as Eq. (11), as reported by Esnault et al.².

\[ \text{MoO}_2^{2+} + 2[RH]_2 = \text{MoO}_2[RH]_2 + 2\text{H}^+, K_{ex} \] (11)

The value of \( K_{ex} \) obtained is shown in Table 1. The extractability of D2EHPA for molybdenum was small compared with that of D2EHPA.

2.2 Extraction of Vanadium

Vanadium species also form various oxo-complex ions in aqueous solutions. Cationic species such as VO₂⁺ are expected to be extracted at the pH region employed when VO₂⁺ is used as feed. However, in the case of D2EHPA, the organic phase and raffinate aqueous sulfate or chloride solutions turned blue during the extraction, whereas the original aqueous phase containing VO₂⁺ was yellow. This indicates that VO₂⁺ in the aqueous phase was reduced to tetravalent vanadium through contact with the organic phase containing D2EHPA. The visible absorption spectra of these solutions showed that the tetravalent vanadium species was VO₂⁺ and all of the feed NaVO₂⁺ was reduced to VO₂⁺ as clearly seen from the characteristic absorbance at a wavelength of 770 nm.

In extraction of vanadium, VO₂⁺ was considered to be extracted. A part of VO₂⁺ exists as VOSO₄ in sulfate solution. The ratio of VO₂⁺ to VOSO₄ existing in the solution was calculated according to the dissociation equilibria of H₂SO₄¹³ and the stability constant of VOSO₄⁹. 

\[ \text{MoO}_2^{2+} + 2[\text{RH}]= \text{MoO}_2\text{[RH]}_2 + 2\text{H}^+, K_{ex} \]
Fig. 5. Effect of concentration of D2EHTPA on distribution ratio of VO$^{2+}$

\[
H_2SO_4 = H^+ + HSO_4^- \quad K_{a1} = 0.4 \text{ M}
\]

(12)

\[
HSO_4^- = H^+ + SO_4^{2-} \quad K_{a2} = 0.012 \text{ M}
\]

(13)

\[
VO^{2+} + SO_4^{2-} = VOSO_4, \beta_{ab} = 10^{2.48} \text{ M}^{-1}
\]

(14)

Two distribution ratios were considered for the sulfate system as follows, one based on total vanadium species and the other on VO$^{2+}$, assuming that $j$-merized complex was formed.

\[
D = j[\underline{V}] / [V]_T, \quad [V]_T = [VO^{2+}] + [VOSO_4]
\]

(15)

\[
D^* = j[\underline{V}] / [VO^{2+}]
\]

(16)

In the chloride system, only VO$^{2+}$ was considered to exist.

A plot of $D^*$ against pH gave a straight line of slope 2 in the sulfate system, whereas the plot of $D$ gave a straight line of slope 2 in the chloride system, as shown in Fig. 4. The plot of $[V] \times [H^+]^2$ against [VO$^{2+}$] at constant D2EHTPA concentration gave a straight line of slope 1, indicating the extracted species were monomeric ($j = 1$). Figure 5 shows the relationship between $D^* \times [H^+]^2$ and $[\underline{LH}_2]^2$, which gives a straight line of slope 1. For the case of a sulfate system, slope analyses were also carried out using VOSO$_4$ as the feed species and similar results were obtained. The extraction equilibrium is thus formulated as follows.

\[
VO^{2+} + \underline{LH}_2 = VOL_2 + 2H^+
\]

(17)

The extraction equilibrium constant, $K_{ex}$, for a VO$^{2+}$ source is $4.5 \times 10^{-2}$ M for the sulfate system when VOSO$_4$ is used as feed. When NaVO$_3$ is used, this is reduced to VO$^{2+}$ during the extraction process. The extraction equilibrium constant is, thus, an apparent value and determined as $K'_{ex} = 8.0 \times 10^{-2}$ M for the sulfate system and $1.6 \times 10^{-3}$ M for the chloride system.

In the case of D2EHPA, no appreciable oxidation or reduction was observed. This established extractant is known to be resistant to oxidation. When NaVO$_3$ was used as feed, the active species was VO$_2^+$. The extraction equilibrium was formulated by slope analyses as follows for the sulfate system.

\[
VO_2^+ + [RH]_2 = VOR_2[RH]_2 + H^+
\]

(18)

$K_{ex} = 4.0 \times 10^{-2}$

When VOSO$_4$ was used as feed, the active species was VO$_3^+$. The equilibrium was as follows for the sulfate system.

\[
VO_3^+ + 2[RH]_2 = VOR_2[RH]_2 + 2H^+
\]

(19)

$K_{ex} = 2.0 \times 10$

This expression is consistent with those reported previously by Sato et al. and Islam et al.
Fig. 8. Variation of performance of vanadium extraction in repeated use of D2EHPA in the case VO$_3^-$ feed.

The effect of loading ratio on extraction equilibrium constant for the sulfate system when VOSO$_4$ is used as feed is shown in Fig. 3(b). The value is constant until a loading ratio of 0.3.

2.3 Separation of molybdenum and vanadium

The effect of pH on the distribution ratios and separation factors for the two metals, obtained with D2EHPA and D2EHPA in the sulfate system, are shown in Figs. 6 and 7, respectively. The extractability of both extractants is nearly the same for Mo, while the extractability of D2EHPA for V(IV) is much greater than that of D2EHPA. Thus, the separation of these metals by D2EHPA is better than that by D2EHPA, especially in the case of separation of Mo and V(IV). D2EHPA is, therefore, more useful for separation of molybdenum and vanadium from low-acidity solutions than D2EHPA.

2.4 Oxidation of D2EHPA by V(V)

D2EHPA is oxidized when the organic phase is contacted with the aqueous phase containing V(V). Figure 8 shows the variation of extraction performance with repeated use of D2EHPA solution. The extractability of vanadium increased with the cycle number when VO$_3^-$ was used as feed, whereas no appreciable increase in extractability was seen when VO$_2^{2+}$ was used as feed. The feed molar ratio of VO$_3^-$ and the extractant was made very large by making the organic and aqueous volume ratio, O/A, as small as 1/5. In this case, extractability of vanadium increased drastically at the second extraction, as shown in Fig. 8(c).

The effect of pH on the distribution ratio and the separation factor of vanadium and molybdenum when using oxidized D2EHPA (after extraction of V(V) two times) is shown in Fig. 6. All of the VO$_3^-$ feed was reduced to VO$_2^{2+}$, even when this extractant was used. Although the extractability of both metals increased with the oxidation of D2EHPA, the separation factor for these metals decreased. Therefore, it is favorable to reduce V(V) to VO$_2^{2+}$ in the aqueous solution prior to extraction and minimize the oxidation of D2EHPA. Selective reduction of pentavalent vanadyl ions was realized by electrochemical exhalation method.

The oxidation of D2EHPA is likely to occur as shown in Eq. (20).

\[ 2[RO]_2P=O]SH + 2VO_2^{2+} + 2H^+ \rightarrow [RO]_2P=O]SSP=O][OR]_2 + 2VO_2^{2+} + 2H_2O \]  

(20)

To confirm this, an extractant containing disulfide was chemically synthesized using dimethyl sulfoxide (DMSO) as an oxidizing agent.

\[ 2[RO]_2P=O]SH + [CH_3]_2SO \rightarrow [RO]_2P=O]SSP=O][OR]_2 + [CH_3]_2S + H_2O \]  

(21)

Analyses of denatured D2EHPA using gas chromatography, gel permeation chromatography, chemical ionization mass spectroscopy and electron impact mass spectroscopy showed that D2EHPA oxidized by VO$_2^{2+}$ was a disulfide.

When D2EHPA oxidized by DMSO was added to the original D2EHPA, the extraction performance increased. In the case where VO$_3^-$ was used as a feed the extraction was more enhanced because of the formation of additional disulfide. When only the oxidized D2EHPA was used as extractant, the extraction of V(V) was similar to that of VO$_2^{2+}$, since a sufficient quantity of disulfide was contained in the oxidized extractant and additional formation of disulfide by V(V) was of little effect. The increase in extractability can, therefore, be attributed to the formation of disulfide or to the synergistic effect of the original D2EHPA and disulfide.

Conclusions

The extraction of molybdenum and vanadium from sulfate and chloride media by bis(2-ethylhexyl)monothiophosphoric acid (D2EHPA) and bis(2-ethylhexyl)phosphoric acid (D2EHPA) was investigated, with the following results obtained.

1) The cationic species of molybdenum, MoO$_2^{2+}$, was extracted by both extractants. The extraction equilibrium reactions were given by Eqs. (7) and (8) for D2EHPA, and by Eq. (11) for D2EHPA.
2) The feed VO$_3^-$ was reduced to VO$^{2+}$ by contact with the organic phase containing D2EHTPA. The extraction scheme of VO$^{2+}$ by D2EHPA is shown in Eq. (17). In the case of D2EHPA, pentavalent and tetravalent vanadium ions were extracted without any oxidation or reduction, and the extraction equilibria are shown in Eqs. (18) and (19), respectively.

3) The separation factor of molybdenum and vanadium by using D2EHTPA was found to be greater than in the case using D2EHPA, especially when VO$_3^-$ was used as feed. Part of the D2EHTPA was found to be oxidized to disulfide by pentavalent vanadium. This enhanced the extractability of molybdenum and vanadium. However, the separation factor of these two elements decreased with the formation of disulfide. Thus, it is important to reduce V(V) to VO$^{2+}$ prior to extraction and minimize the oxidation of D2EHTPA for efficient separation and repeated use of the extractant.

**Nomenclature**

- $D$ = distribution ratio based on total aqueous metal species
- $D'$ = modified distribution ratio based on metal species active for the extraction
- $j$ = degree of aggregation of extracted species
- $K$ = equilibrium constant of metal species in aqueous solution
- $K_d$ = dissociation constant of sulfuric acid
- $K_{ex}$ = extraction equilibrium constant
- $K_{ex}$ = apparent extraction equilibrium constant in the case of NaVO$_3$ used as feed
- LH = monomer of D2EHTPA

$M$ = mol/dm$^3$

RH = monomer of D2EHPA

$\beta_{alt}$ = stability constant of vanadyl sulfate [M$^{-4}$]

$[\ ]$ = concentration of species in brackets [M]

- = organic phase species

**Literature Cited**