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Short communication

Extraction of V(V), Mo(VI) and W(VI) polynuclear species by primene JMT

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Abstract

Elements Mo(VI), W(VI) and V(V), polymerize at low pH (within the approximate pH range 2–6) to form polyanions $Mo_7O_{24-n}(OH)_n{}^{(6-n)-}$ (n=0, 1, 2, 3), $W_{12}O_{41-2n}{}^{(10-4n)-}$ (n=0, 1) and $V_{10}O_{28-n}(OH)_n{}^{(6-n)-}$($n$=0, 1, 2). Extraction of these complex species leads to the high ratio of the concentration of metal and amine in the organic phase. Quantitative information on the possibility of extracting V(V), Mo(VI), and W(VI) from sulphate solutions by primary amine Primene JMT with respect to initial concentration of metals and sulphuric acid are presented.

Experimental results confirmed the advantage of Mo, W and V extraction by primary amine from sulphuric acid solutions mainly within the range of pH in which the polymeric anionic complexes are present. It was found that several equilibrium reactions must be taken into account. The reaction of amine salts forming, anion exchange reactions and in case of sulphate groups absence probably addition reactions take place.

Primary amine Primene JMT contrary to tertiary amines enables effective extraction also from weak acidic solutions. It was concluded that the behaviour of all the three elements studied is very similar.

Keywords: Primary amine primene JMT; Vanadium; Molybdenum; Tungsten; Extraction

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1. Introduction

Aqueous solutions containing vanadium, molybdenum and tungsten are encountered in a variety of industrial processes.

One of the major industrial separation problems that can be solved by solvent extraction is the processing of uranium and vanadium from acid sulphate leach liquors. The possibility of extracting V(V) and U(VI) by using quaternary ammonium salts was first mentioned by Clifford [1]. The recovery of molybdenum by solvent extraction deals also mainly with its removal from uranium circuits [2–4]. Many methods of extracting molybdenum and tungsten have been described in the literature [5–9]. Separation and purification of vanadium and molybdenum by tri-*n*-octylmethylammonium chloride and subsequent selective stripping were published elsewhere [10,11]. Equilibrium data for the system Aliquat 336-vanadium and chromium were reported by Hughes and Leaver [12]. Anion exchange as the extraction mechanism was proposed for the extraction of V(V) by tri-*n*-octyl [13], tri-*n*-capryl, tri-*n*-nonyl and tri-isononylamine [14]. Extraction of Mo(VI) by tri-*n*-octylamine from strong acid solutions was also investigated [15]. Extraction processes for the efficient separation and recovery of V(V) from spent hydrodesulphurization catalysts have been recently of interest [16,17]. Separation of W from acid solutions using Alamine 336 was studied by Kim and Chiola [18]. Yun [19] suggested a mathematical model for extraction of W(VI) by tertiary amines.

It is obvious that the extraction of V, Mo, W from aqueous solutions by various types of high-molecular amines have already been investigated under different conditions. The published reviews describe mainly the extraction by tertiary amines or quaternary ammonium reagents and amine extraction was usually investigated with respect to practical application. Less attention has been paid to the extraction by primary amines and the mechanism of the process occurs in literature only in a unique case [7,8].

We have published some results on polyvanadates [20], polymolybdates [21,22] and polytungstates [23] extraction by primary amine Primene JMT.

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This paper describes some experimental results comparing the extraction of above mentioned polyanions from aqueous sulphuric acid solutions by primary amine Primene JMT.

2. Equilibria in the aqueous phase

Equilibria involving $MoO_4{}^{2-}$ protonation are described as [24]:

$$7MoO_4{}^{2-} + (8+n)H^+ = Mo_7O_{24-n}(OH)_n{}^{(6-n)-} + 4H_2O, (n = 0, 1, 2, 3)$$

and the polymolybdates are formed quite rapidly.

Under low concentration of Mo monomeric forms are formed

$$MoO_4{}^{2-} + kH^+ = H_kMoO_4{}^{(2-k)-}, \quad (k = 1, 2)$$

With a minimum solubility occurring at about pH 1.5, crystalline MoO_3 is in the equilibrium with $MoO_4{}^{2-}$

$$MoO_4{}^{2-} + 2H^+ = MoO_3(s) + H_2O$$

A schematic diagram for Mo(VI)–OH$^-$ species is shown in Fig. 1.

Tungsten behaves similarly [24]:

$$12WO_4{}^{2-} + (14+4n)H^+ = W_{12}O_{41-2n}{}^{(10-4n)-} + (7+2n)H_2O, \quad (n = 0, 1)$$

$$6WO_4{}^{2} + 7H^+ = H_kWO_4{}^{(2-k)-}, \quad (k = 1, 2)$$

The equilibrium constants for above mentioned reactions as well as for Mo equilibria are published in literature [6,24]. Similarly as to Mo, crystalline WO_3 precipitates in the pH region ~2. The possibility of forming further polyanions $W_{12}O_q(OH)_r{}^{v-}$, where v varies between 20 and 0, is also described in the literature [6,18]. It is, however, more likely that these species are only the transient species formed in the course of the polymerization processes. Schematic diagram for W(VI)–OH$^-$ species is shown in Fig. 2.

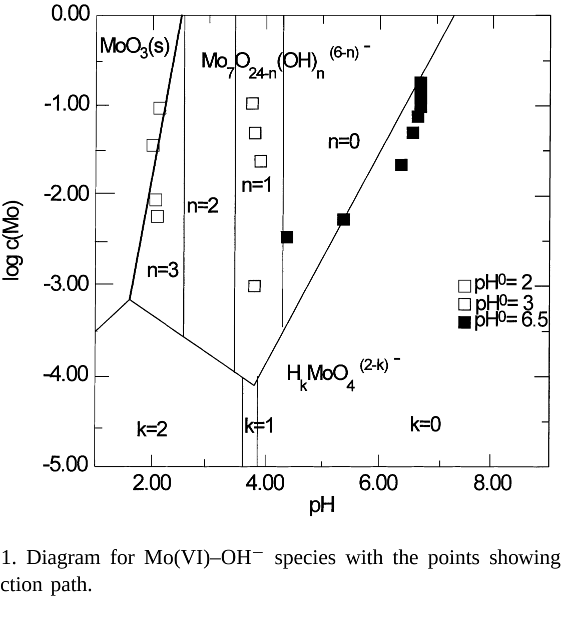

Fig. 1. Diagram for Mo(VI)–OH$^-$ species with the points showing the extraction path.

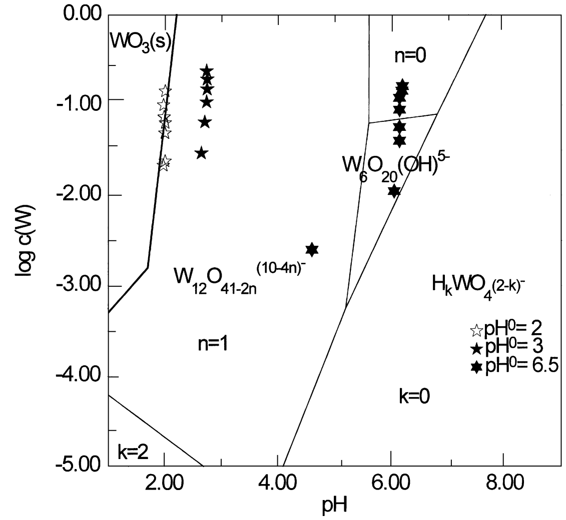

Fig. 2. Diagram for W(VI)–OH$^-$ species with the points showing the extraction path.

Polymeric species of V(V) are formed by hydrolysis of $VO_2{}^+$ cation [24]

$$10VO_2{}^+ + 8H_2O = V_{10}O_{28-n}(OH)_n{}^{(6-n)-} + (16-n)H^+, \quad (n = 0, 1, 2)$$

and monomeric species by reaction

$$VO_2{}^+ + 2H_2O = VO_{4-m}(OH)_m{}^{(3-m)-} + (4-m)H^+, \quad (m = 0, 1, 2, 3)$$

It is supposed that in the region between decavanadates and monomeric species, the formation of $V_kO_{3k}{}^{k-}$ occurs

$$kVO_2{}^+ + kH_2O = V_kO_{3k}{}^{k-} + 2kH^+, \quad (k = 3, 4)$$

and above a pH of 8 the pyrovanadates $V_2O_7{}^{4-}$ appear.

A schematic diagram showing the regions of predominance of the vanadium species is in Fig. 3.

At low values of pH the solid oxide precipitates

$$2VO_2{}^+ + H_2O = V_2O_5 + 2H^+$$

The equilibrium constants are available in the literature [24]. The data differ in dependence on experimental conditions (ionic strength, medium).

Generally, in all cases the anions in the aqueous phase can be expressed in the form $Me_pO_q(OH)_r{}^{v-}$, where Me=Mo(VI), W(VI), V(V).

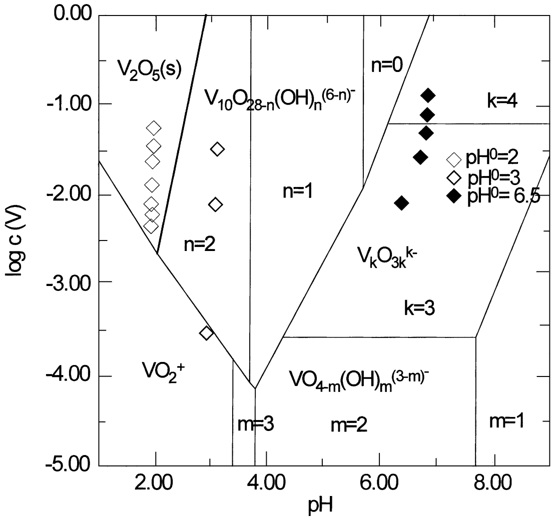

Fig. 3. Diagram for V(V)–OH$^-$ species with the points showing the extraction path.

3. Experimental

PRIMENE JMT-RNH$_2$-(R=(CH$_3$)$_3$C(CH$_2$C(CH$_3$)$_2$)$_4$ [29,30]) (Rohm & Haas) was diluted to ~0.1 M solution in benzene with 5% of *n*-octanol. Amine was preequilibrated with sulfuric acid in molar ratio 2:1, to form the amine sulphate.

The stock solutions of molybdenum (VI), tungsten and V(V) were prepared by dissolving (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O, Na$_2$WO$_4$·2H$_2$O and NaVO$_3$ in sulphuric acid of required concentration (pH^0=2, 3, 6.5).

The equal volumes of organic and aqueous phase were equilibrated in a shaker at the temperature (20±2)°C for 10 min (it has been previously established that equilibrium was achieved within this time). The concentration of molybdenum in the aqueous phase was determined by titration with Ce(SO$_4$)$_2$ or by AAS, the concentration of tungsten was determined gravimetrically or spectrophotometrically and concentration of vanadium in aqueous phase was determined by titration with Fe^{2+} salt or spectrophotometrically. The concentration of sulphate ions in aqueous and organic phase was determined by titration with BaClO$_4$ (sulphonazo III as indicator). The value of initial and equilibrium pH in aqueous phase was measured using a pH-meter.

4. Extraction equilibria

The formation of amines salts (ion-pairs) is required at amine extraction. The protonation of amine in sulphuric acid solutions gives sulphates or bisulphates [25,26]:

$$2\mathrm{A}^{\mathrm{org}} + \mathrm{H_2SO_4}^{\mathrm{aq}} = (\mathrm{AH})_2\mathrm{SO_4}^{\mathrm{org}} \tag{1}$$

$$(\mathrm{AH})_2\mathrm{SO_4}^{\mathrm{org}} + \mathrm{H_2SO_4}^{\mathrm{aq}} = 2\mathrm{AH}\cdot\mathrm{HSO_4}^{\mathrm{org}} \tag{2}$$

With increasing concentration the aggregation (dimerization) of bisulphate occurs and sometimes the excess acid extraction is described [25,26].

The basic mechanism of amine extraction is an anion exchange reaction [27]. In case of the extraction by amine sulphate and supposing that commonly expressed anions $\mathrm{Me}_p\mathrm{O}_q(\mathrm{OH})_r{}^{v-}$ are present in the aqueous phase, the reaction:

$$\mathrm{Me}_p\mathrm{O}_q(\mathrm{OH})_r{}^{v-} + 0.5v(\mathrm{AH})_2\mathrm{SO_4} = (\mathrm{AH})_v\mathrm{Me}_p\mathrm{O}_q(\mathrm{OH})_r + 0.5v\mathrm{SO_4}^{2-} \tag{3}$$

proceeds. Extraction of neutral molecules can also proceed in case that the anion of amine salt and the anion passing from the aqueous phase are equal [25,27]. In our case:

$$\mathrm{H}_v\mathrm{Me}_p\mathrm{O}_q(\mathrm{OH})_r + x(\mathrm{AH})_v\mathrm{Me}_p\mathrm{O}_q(\mathrm{OH})_r = \mathrm{H}_v\mathrm{Me}_p\mathrm{O}_q(\mathrm{OH})_r[(\mathrm{AH})_v\mathrm{Me}_p\mathrm{O}_q(\mathrm{OH})_r]_x \tag{4}$$

The analogous reactions with bisulphate are also suggested [19].

According to the stoichiometry in Eq. (3) the ratio of metal and amine $c_{\mathrm{Me}}{}^{\mathrm{org}}/c_{\mathrm{A}}$ in the saturated organic phase is

$$\frac{c_{\mathrm{Me}}{}^{\mathrm{org}}}{c_{\mathrm{A}}} = \frac{p}{v} \tag{5}$$

Analogously, for the relation between the concentration of SO$_4$ group and metal in the organic phase follows:

$$-S = \frac{-\Delta c_{\mathrm{SO_4}}{}^{\mathrm{org}}}{\Delta c_{\mathrm{Me}}{}^{\mathrm{org}}} = 0.5\frac{v}{p} \tag{6}$$

5. Results and discussion

Three levels of the initial pH values were chosen for the investigation. The lowest pH^0=2 corresponds with the boundary of solid oxides precipitation. The highest pH^0=6.5 corresponds with the boundary of polymeric species forming. The medium value pH^0=3 should be the most suitable region for extraction.

Figs. 4–6 show the extraction isotherms for above mentioned pH^0 values. Diagrams are complemented with the dash-lines that mark the theoretical composition of complexes according to the Eq. (5). The diagrams show very advantageous extraction equilibria. The low concentrations of metals are almost completely extracted into organic phase. As the concentration of metals enhances the loaded organic phases were found.

Isotherms in Figs. 4–6 are measured at the constant initial pH values. The pH in the equilibrium depends on the metal concentration. Equilibrium pH values for the very low concentrations of metals are within the range 2–3 regardless the starting values. In this case the influence of the reactions (1) and (2) prevails. In case of higher concentration of extracted metals the equilibrium pH are almost the same as their initial value.

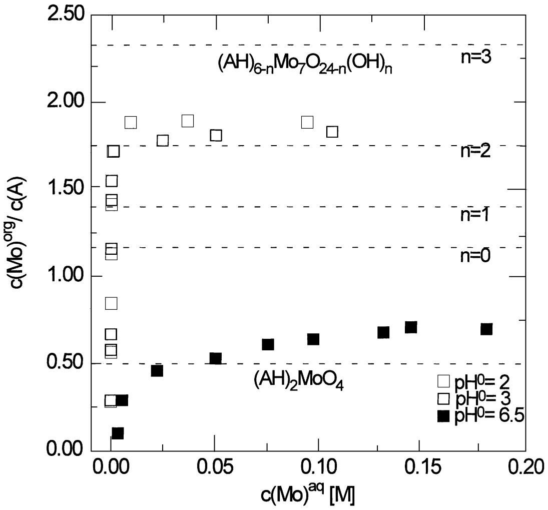

Fig. 4. Isotherms for extraction of molybdenum.

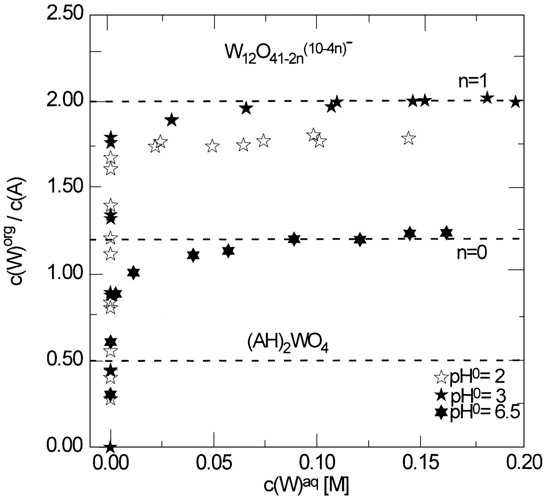

Fig. 5. Isotherms for extraction of tungsten.

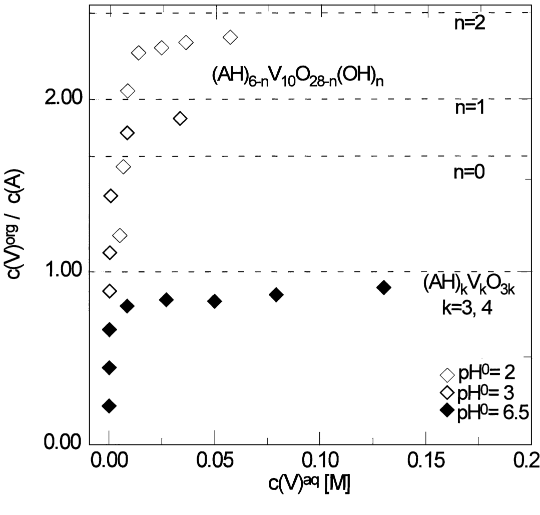

Fig. 6. Isotherms for extraction of vanadium.

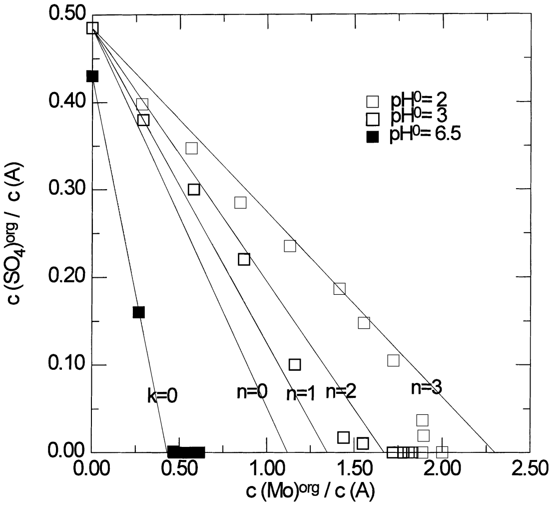

Fig. 7. Equilibrium molar ratios SO_4^{2-}/A vs. Mo/A.

The pH values and corresponding concentration of metals (only for points with $c_{Me}>10^{-4}$ M) in equilibrium are plotted in Figs. 1–3. It is obvious that the extraction path for higher pH values can cross over several regions with various prevailing species. The experimental points for pH∼2 (in Figs. 1–3) lie at the boundary of solid phase precipitation. This fact is manifested in Figs. 4–6 with lower concentration of metals in organic phases. The loading of organic phases does not correspond with transfer of supposed complexes.

The concentrations of metals and sulphate groups in organic phase are plotted experimental points in Figs. 7–9. The lines corresponding with anion exchange according to the Eq. (3) are drawn as well. The slopes of lines are in accordance with Eq. (6) for individual supposed complexes. In most cases the experimental points approach some of the lines. It is evident that parallel to the anion exchange the reactions (1) and (2) must be considered. Figures also show that in most cases the loading of organic phase continues

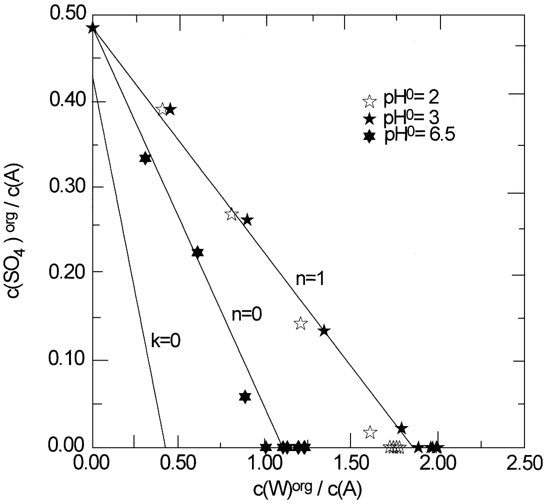

Fig. 8. Equilibrium molar ratios SO_4^{2-}/A vs. W/A.

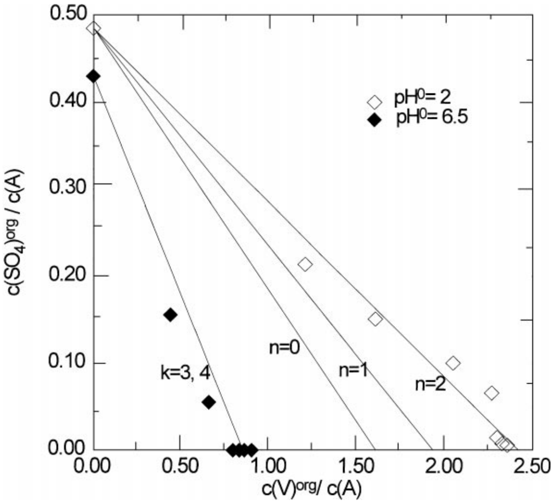

Fig. 9. Equilibrium molar ratios SO_4^{2-}/A vs. V/A.

also at the absence of sulphate groups in the organic phase. Another extraction mechanism must be applied, likely addition according to the Eq. (4). A considerable change of equilibrium pH values accompanies the change of extraction mechanism mainly for extraction at higher initial pH (Figs. 1–3). This change is also in agreement with Eq. (4).

6. Conclusions

Experimental results confirmed the advantage of Mo, W and V extraction by primary amine from sulphuric acid solutions mainly within the range of pH in which polymeric anionic complexes are present. It was found that several equilibrium reactions must be taken into account. The reaction of amine salts forming, anion exchange reactions and in case of the absence of sulphate groups probably additional reactions take place. Primary amine Primene JMT enables extraction from weak acidic solutions. The behaviour of all three studied elements is very similar.

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