

Extraction of Cr(VI), Mo(VI), and W(VI) from Sulfate Solutions by Primary Amine*

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The results of extraction of Cr(VI), Mo(VI), and W(VI) from solutions containing sulfuric acid have been presented in this work. The paper follows up our previous works dealing with the mechanism of Mo(VI) and W(VI) salts extraction by primary amine Primene JM-T. The aqueous solutions with pH 3 were chosen for the comparison of the mechanism of extraction of polynuclear species of studied elements. Experimental results confirmed that the basic extraction mechanism was an anion exchange. The advantage of Cr(VI), Mo(VI), and W(VI) extraction, within the range of pH in which the polymeric anionic complexes are present, was acknowledged. The possibility of application of Primene JM-T for the extraction of studied metals in a broad range of acidity was also investigated.

Metal ion extraction through complexation with an organic soluble ligand is a process widely used in the hydrometallurgical industry for the separation, purification, and recovery of many metals. Amine extraction of Cr(VI), Mo(VI), and W(VI) from the diluted solutions is usually performed from acidic media, mainly from sulfuric and hydrochloric acid. The formation of polynuclear species (dichromates, heptamolybdates, and dodecatungstates) [1] is exploited for the higher loading of the organic phase.

The recovery of molybdenum by solvent extraction deals mainly with its removal from uranium circuits [2–4]. Several methods of separating molybdenum and rhenium [5–8] and molybdenum and tungsten [9–12] have been published. Extraction of molybdenum from strong acidic solutions has been studied in works [13–17].

The first works dealing with the extraction of tungsten were also connected with the study of uranium. Several works studying the extraction from acidic solutions [15, 18–22] and mathematical modeling of extraction isotherms by tertiary amines [23] were published. The influence of temperature on separation coefficient was explained by the change of the aqueous phase composition [24].

The separation of chromium(VI) from industrial wastewaters is of great interest mostly due to the high

toxicity of this metal. Chromium from the acidic solutions can be extracted by tertiary amines R_3N , secondary amines R_2NH , and primary amines RNH_2 or their salts, respectively. Results with tertiary amines are published most frequently [25–29], however, less attention is paid to the secondary [28] and primary amines [30]. Extraction from sulfuric acid is usually studied but the hydrochloric acid is mentioned as well [31]. Quaternary ammonium salt is applied for the Cl^- and OH^- medium [32, 33].

The most frequently utilized tertiary amines are trioctylamine (TOA) and Alamine 336. Benzene, xylene, carbon tetrachloride, and kerosene, usually with the addition of C_6 – C_{10} alcohols as the modifiers, are employed as diluents. The experiments with secondary amine dinonylamine, Amberlite LA-2, primary amine N 1923 and Primene JM-T were also published. Quaternary ammonium salt Aliquat 336 is frequently used for extraction from neutral and alkaline solutions. The exchange of an anionic species of studied metals and an anion of amine salt is supposed to be the mechanism of extraction.

We have published the results of the extraction of Mo(VI) from the sulfuric acid solutions [34], extraction of Mo(VI) and V(V) [35], and extraction of W(VI) [36] by primary amine Primene JM-T.

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EXPERIMENTAL

Batch experiments were carried out by agitating organic with aqueous feed in a separatory funnel for 10 min. The organic phase consisted of approximately 0.1 mol dm⁻³ solution of Primene JM-T (Rohm & Haas) in benzene and 5 vol. % of octan-1-ol as the modifier. Primene JM-T is primary aliphatic amine with highly branched alkyl chains in which the amino nitrogen atom is linked to a tertiary carbon to give the *t*-alkyl grouping. It consists of mixtures of isomeric amines in the C 16–22 range.

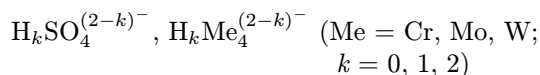
Amine was converted into amine sulfate before extraction of metals. The aqueous feed consisted of Cr(VI) as K₂Cr₂O₇, Mo(VI) as (NH₄)₆Mo₇O₂₄ · 4H₂O, W(VI) as Na₂WO₄ · 2H₂O. H₂SO₄ was used for pH adjustment. Total chromium content in the aqueous phase was measured by the titration with Fe(II) salt, molybdenum content in the aqueous phase was determined by the titration with Ce(SO₄)₂ [37, 38], tungsten determination, in the aqueous phase, was obtained gravimetrically as WO₃ or by spectrophotometric method with thiocyanate [39]. The metal content in the organic phase was not measured directly but calculated on the basis of mass balance on the metals content in the aqueous phase before and after each experiment. The check analysis of the organic phase was done after stripping with 10 % of NaHCO₃.

The concentration of sulfate ions in the organic phase was determined by titration with BaClO₄ (sulfonazo III as indicator).

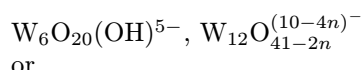
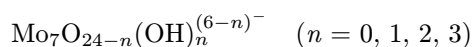
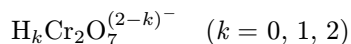
THEORETICAL

Equilibria in the Aqueous Phase

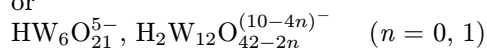
The presence of various types of anionic or neutral forms is expected in sulfuric acid medium depending on pH and on the concentration of metals. Simple anionic or neutral forms



occur at lower and polymeric forms



or



at higher concentration of metals. The equilibrium constants of protonation and polymerization reactions are available in the literature [1, 40, 41]. The literature also reports the presence of the species

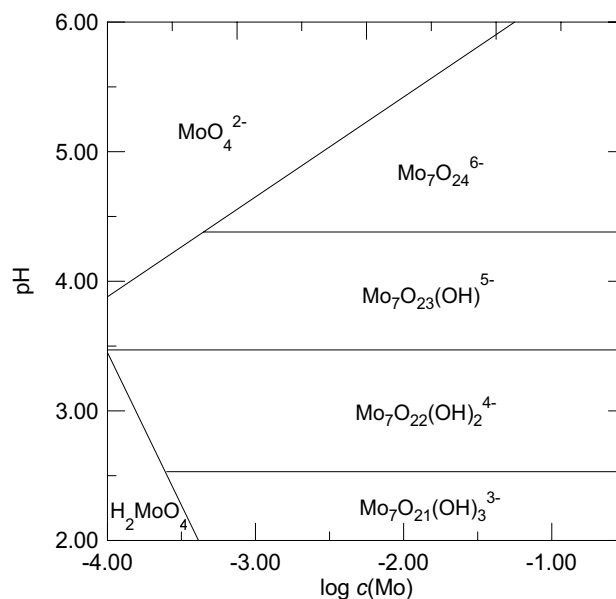


Fig. 1. Diagram for Mo(VI)—OH⁻ species (according to [1]).

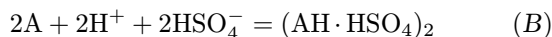
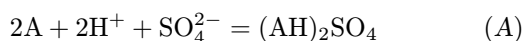
CrO₄(SO₃)₂²⁻ [1, 41], Mo₈O₂₆⁴⁻ [15, 16], Mo₁₉O₅₉⁴⁻ [1], and W₃O₁₁⁴⁻, H₄W₃O₁₃³⁻ [18] in solutions at pH < 2. The existence of polymeric anions W₁₂O₄₀⁸⁻, W₁₂O₄₆²⁰⁻, [18], metatungstates H_m[H₂W₁₂O₄₀]^{(6-m)-}, and paratungstates H_m[H₂W₁₂O₄₂]^{(10-m)-} (m = 0, 1, 2, 3) [12] is also supposed in solutions at higher pH's. The neutral forms of hydrated oxides MeO₃ · wH₂O (Me = Mo, W) are precipitated from the solutions at pH approximately 1.5 [1, 12, 15, 18]. Molybdenum occurs also as a cation MoO₂²⁺ in strong acidic solutions (pH < 1) [2, 15, 17].

If we narrow the field of our attention to the interval of pH 2–5, the prevailing form of sulfuric acid is SO₄²⁻ [29], the prevailing form of Cr(VI) is HCrO₄⁻ (for c(Cr) < 0.01 mol dm⁻³) and Cr₂O₇²⁻ (for c(Cr) > 0.01 mol dm⁻³) [1]. Molybdenum occurs mainly in the form of heptamers and Fig. 1 shows the regions of predominance of the various species [1]. Metatungstates W₁₂O₃₉⁶⁻ or H₂W₁₂O₄₀⁶⁻ are dominant according to [1] in the range of pH 2–5 and at c(W) > 0.0001 mol dm⁻³. Kim *et al.* [18] give evidence of the existence of these species only in the region of pH 2.4–3.4 and Voldman [12] within the range of pH 2–4. In solutions with pH > 4 [12] or pH > 4.2 [18] the authors suppose the presence of paratungstates H₂W₁₂O₄₂¹⁰⁻ or H₁₀W₁₂O₄₆¹⁰⁻ and HW₆O₂₁⁵⁻ (for lower concentrations of W). If the concentration c(W) < 10⁻⁵ mol dm⁻³ mononuclear WO₄²⁻ prevails [1].

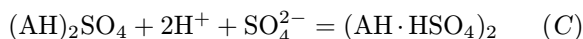
Reactions with Amine and its Salts

Amines (A) themselves do not extract metals, the formation of their salts is required [42]. Sulfuric acid reacts with amine by formation of sulfate (AH)₂SO₄ and hydrogensulfate AH · HSO₄. The amine hydrogen-

sulfate can form the dimer $(\text{AH} \cdot \text{HSO}_4)_2$ [18]. The process is described by reactions [23]

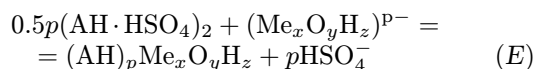
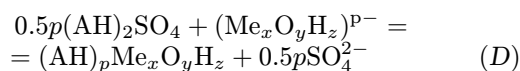


Reaction (B) can be written also as [43]

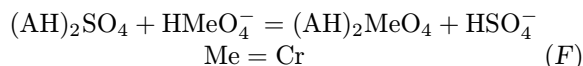


According to the study of Kim [44] the prevailing form is $(\text{AH})_2\text{SO}_4$ till the equilibrium concentration of sulfuric acid in the aqueous phase reaches the value 0.02 mol dm^{-3} . If hydrogensulfate prevails, then the share of free amine is negligible.

The anion-exchange mechanism is assumed for the extraction of metal complexes ($\text{Me} = \text{Cr}, \text{Mo}, \text{W}$) according to the common reactions



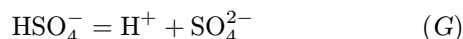
Only one exception was found in the literature [29] whereby for the extraction of chromium the following reaction was proposed



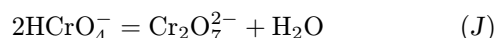
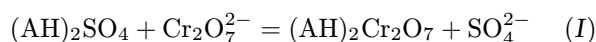
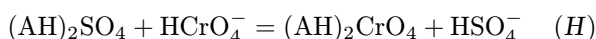
The reliability of eqn (E), where the extraction by hydrogensulfate is supposed, is uncertain.

Extraction Equilibria

If we study only solutions within pH 2–4, then on the basis of data from the literature we can expect an equilibrium among amine, amine sulfate, and amine hydrogensulfate (eqns (A), (B)) together with the equilibrium in the aqueous phase

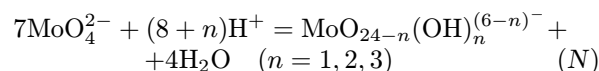
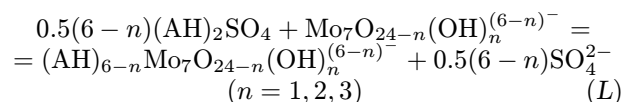
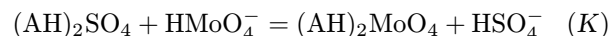


Extraction of chromium can be described considering eqn (F) together with anion exchange (eqn (D)) and equilibrium in the aqueous phase

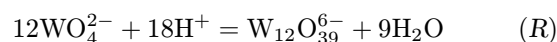
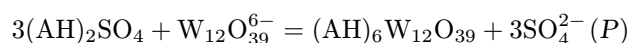
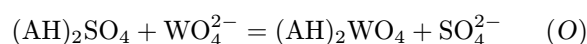


For the extraction of molybdenum we can consider eqn (F) for the extraction of HMoO_4^{2-} , anion exchange

(eqn (D)) and equilibrium in the aqueous phase



Analogously, the extraction of tungsten can be described by eqn (F) for HWO_4^- species, anion exchange according to eqn (D) and equilibrium in the aqueous phase



RESULTS AND DISCUSSION

The results of experiments are presented in Fig. 2 as a distribution diagram for the solutions with initial pH 3. The advantage of the extraction of metals in a form of polynuclear species is obvious. The ratio $c(\text{Me})/c(\text{A})$ in the organic phase exceeds the value 0.5,

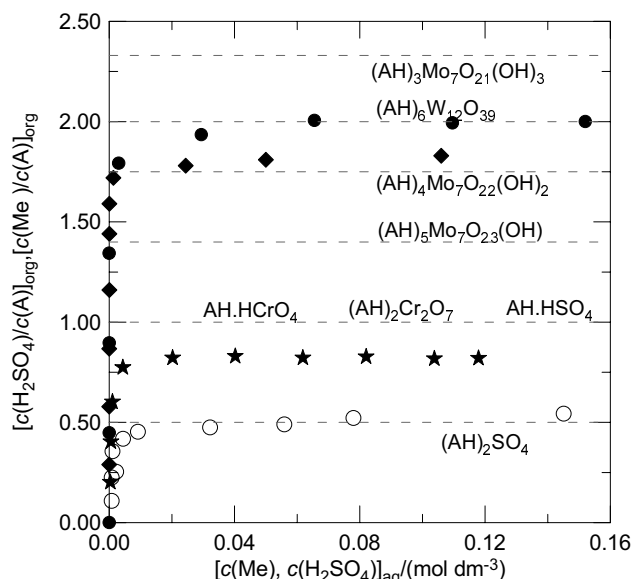


Fig. 2. Distribution diagrams. \circ H_2SO_4 , \bullet W, \blacklozenge Mo, \star Cr.

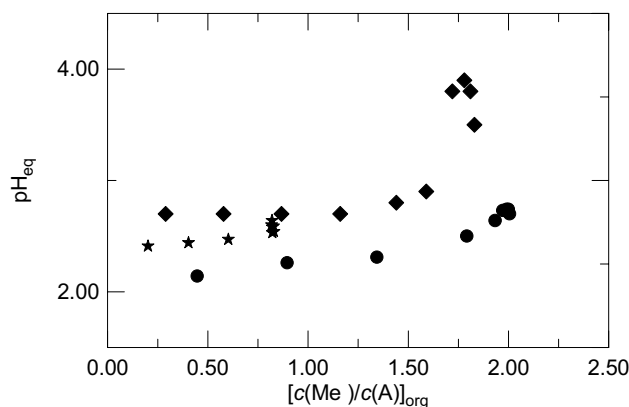


Fig. 3. The dependence of equilibrium pH in the aqueous phase on the concentration of metals in the organic phase ($\text{pH}_0 = 3$). ● W, ◆ Mo, ★ Cr.

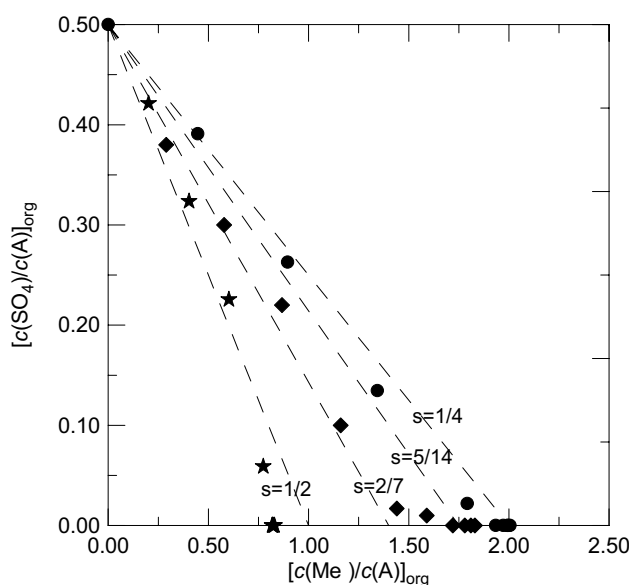


Fig. 4. The dependence of SO_4^{2-} concentration in the organic phase on the loading of organic phase with metals ($\text{pH}_0 = 3$). ● W, ◆ Mo, ★ Cr.

which could correspond to the extraction of MeO_4^{2-} . The diagram shows also very advantageous extraction at low concentrations of extracted species.

The curve for extraction of chromium shows that when the concentration of metal was higher, the extracted species were ions $\text{Cr}_2\text{O}_7^{2-}$ even though the full saturation of the organic phase was not achieved. The isotherm for molybdenum shows that the concentration of Mo(VI) in the organic phase is higher than concentration in the expected complex $(\text{AH})_4\text{Mo}_7\text{O}_{22}(\text{OH})_2$. The isotherm for tungsten confirms the theoretical assumption. The distribution of sulfuric acid shows that at low concentrations of acid amine sulfate and free amine are in equilibrium.

Fig. 3 shows that the change of equilibrium pH in the aqueous phase is dependent on the saturation

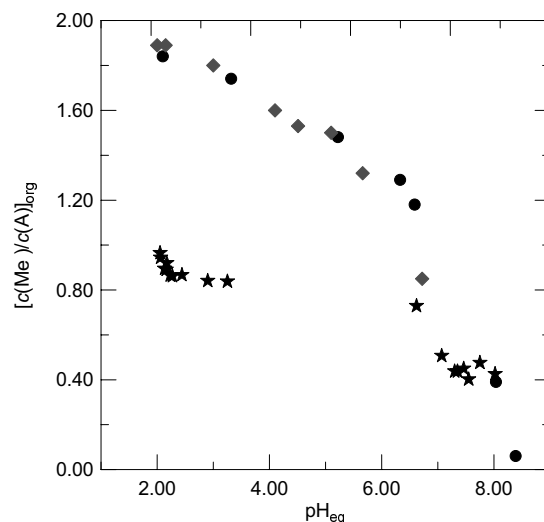


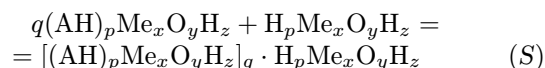
Fig. 5. The loading of organic phase in dependence on equilibrium pH. ● W, ◆ Mo, ★ Cr. $c(\text{W})_0 = 0.3 \text{ mol dm}^{-3}$, $c(\text{Mo})_0 = 0.25 \text{ mol dm}^{-3}$, $c(\text{Cr})_0 = 0.16 \text{ mol dm}^{-3}$.

of the organic phase. Most of the experimental points have $\text{pH} < 3$ ($\text{pH} 3$ was the initial acidity of solutions). This tendency is evidently caused by the balancing of concentrations of free amine, amine sulfate in the organic and SO_4^{2-} and HSO_4^- in the aqueous phase. The change should be more evident at lower concentrations of metals. The differences between metals are caused by unequal initial concentrations of amine and sulfates.

The expected anion exchange is confirmed by the results depicted in Fig. 4. The saturation of the organic phase with metals is accompanied with a decrease in sulfate groups. Fig. 4 is complemented with the lines having the slope $s = [\Delta c(\text{SO}_4)/\Delta c(\text{Me})]_{\text{org}}$.

If only the anion exchange took place then for the exchange of $\text{Cr}_2\text{O}_7^{2-}$ s would be $-1/2$ according to eqn (I), $-2/7$ for $\text{Mo}_7\text{O}_{22}(\text{OH})_2^{4-}$ according to eqn (N), $-5/14$ for $\text{Mo}_7\text{O}_{23}(\text{OH})^{5-}$ and for the exchange of $\text{W}_{12}\text{O}_{39}^{6-}$ s would be $-1/4$ according to eqn (P). The experimental points in Fig. 4 are in agreement with expected slopes mainly at lower concentration of metals. The displacement of SO_4^{2-} from the organic phase was confirmed in all experiments.

Figs. 3 and 4 show the existence of conditions when the extraction of Mo and W cannot be performed by anion exchange. The concentration of metals in the organic phase increases also in the absence of SO_4^{2-} in the organic phase. In this situation, the extraction can be performed only by the addition of neutral molecules, for example $\text{H}_5\text{Mo}_7\text{O}_{23}(\text{OH})$ or $\text{H}_6\text{W}_{12}\text{O}_{39}$, to the complex in organic phase



This mechanism is not in contradiction with com-

mon knowledge of amine extraction [42, 45]. The transfer of the above-mentioned neutral molecules is accompanied by the increase of pH (Fig. 4).

Fig. 5 illustrates the extraction ability of Primene JM-T. The effective extraction can be performed within a broad range of pH, which represents an asset of this extractant.

CONCLUSION

Experimental results confirmed the advantage of Cr(VI), Mo(VI), and W(VI) extraction by primary amine from sulfuric 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 formation of amine salts, anion-exchange reactions, and in the absence of sulfate groups probably also additional reactions. It was ascertained that the behaviour of all three studied elements is very similar and primary amine Primene JM-T enables extraction also from weak acidic solutions.

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