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Speciation of Molybdenum (VI) In Aqueous and Organic Phases of Selected Extraction Systems

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Abstract: The extraction study of molybdenum (VI) by 30% tri-*n*-butyl phosphate in *n*-dodecane and 0.2 M octyl (phenyl)-N,N-di-isobutylcarbamoylmethylphosphine oxide in 30% tri-*n*-butyl phosphate extraction systems was performed from aqueous solution containing HCl, HNO_3 and acetohydroxamic acid. Depending on extraction conditions, acetohydroxamic acid can significantly affect the speciation of molybdenum and can increase or decrease its distribution ratio. Our investigation confirmed the strong ability of the acetohydroxamic acid to form complexes with Mo even in highly acidic solutions. UV absorption spectra confirmed that a fraction of the Mo(VI)-AHA species can be present in the organic phase after extraction.

Keywords: Acetohydroxamic acid; CMPO; Extraction; Molybdenum, PUREX; speciation; TBP; TRUEX; UV-Vis spectroscopy

INTRODUCTION

The main goal of the advanced separation programs is to develop a method for effective separation of actinides and fission products which will reduce both the cost and environmental impact of reprocessing irradiated nuclear fuel in the future. To meet these criteria, a suite of solvent extraction processes, "UREX+" is being developed (1). The first extraction step, UREX, is based on application of 1.1 M (30%) tri-*n*-butyl phosphate (TBP) in n-alkane and nitric acid solutions of spent nuclear fuel (PUREX), and the acetohydroxamic acid (AHA, Fig. 1) is added into scrub streams to improve the separation of uranium, and prevent

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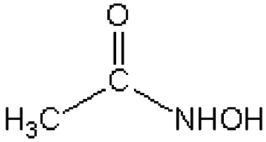


Figure 1. Acetohydroxamic acid.

the extraction of plutonium and neptunium by either their reduction or complexation into non-extractable species (2). At the next separation step, the UREX-solvent is turned into the TRUEX-solvent by adding the second extraction agent octyl(phenyl)-N,N-di-isobutyl-carbamoyl-methylphosphine oxide (CMPO) (3–5), which was designed for selective extraction of transuranium elements from the spent nuclear fuel solution. While the distribution behavior of actinide elements in the UREX and TRUEX processes has been studied in great detail, behavior and speciation of molybdenum and other fission products present in relatively high chemical concentrations in the dissolved spent nuclear fuel is still not well known. Several studies have been performed on the distribution behavior of molybdenum by PUREX and TRUEX solvents (6,11).

Content of Mo in spent nuclear waste streams should be carefully controlled. It is very important due to the scavenging of significant amounts of uranium and plutonium to precipitates of molybdenum: $UO_2Mo_2O_7.(1–3)H_2O$, $(PuMoO_4)_2H_2O$ (12). In the present paper, we focus on the speciation behavior of molybdenum (VI). Results from distribution experiments are compared with data from spectrophotometric measurements and formation of various molybdenum species in both aqueous and organic extraction phase is discussed.

EXPERIMENTAL

Methods

The distribution ratio of molybdenum was determined using the radioactive tracer ^{99}Mo obtained by neutron activation of ~150 mg of molybdenum trioxide in the OSU TRIGA Reactor. An activated sample of molybdenum oxide was dissolved in 1 M NaOH, then added to relevant acid (HCl, HNO_3) and diluted to desired concentration. A spike providing a constant concentration of metal $[Mo] = 1.07 \times 10^{-3}$ M was added to each extraction vial.

The extraction of hexavalent molybdenum was performed from hydrochloric acid solutions with tri-*n*-butyl phosphate (TBP, 30 vol. % in *n*-dodecane) and from nitric acid with 0.2 M octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) dissolved in 30 vol. % TBP in *n*-dodecane. Equal volumes of organic and aqueous phases were vigorously agitated (VORTEX) for 4 minutes. Phases were separated after a short centrifugation, and aliquots from both the organic and aqueous phases were taken for γ-spectrometric counting to determine the molybdenum distribution ratios. The extraction procedure was repeated with a fresh portion of aqueous phase. The reported distribution ratios are average values from at least two extractions.

UV-Vis absorption spectra were collected using 1 cm quartz cuvette and the Ocean Optics QE65000 spectrophotometer with a resolution of 0.8 nm. All spectra were taken against the blank solution, which was identical to the measured sample except the component of interest.

RESULTS AND DISCUSSION

Complexes of Molybdenum (VI) with Oxygen Donor Atoms

The aqueous chemistry of Mo(VI) is quite complicated due to the rich coordination chemistry of this transition metal. Mo(VI) has a pronounced affinity for the oxygen atom (13) and tends to form a variety of oxo-complexes which represent the overwhelming majority of Mo(VI) coordination compounds (14). The structure and reactivity of Mo(VI) oxo-complexes are determined (15) by the number and type of coordinated oxygen atoms or their protonated forms. Among cations having the *d*0 electronic configuration, Mo(VI) forms both tetrahedra $MoO_4^{2-}$and octahedra MoO_6. Transition metal atoms in higher oxidation states very frequently form bi- and polynuclear species with bridging oxygen atoms. Characteristic structures of oxo-complexes of Mo(VI) are given in Fig. 2. Terminal oxygen atoms are arranged in the *cis* position relative to each other. This structure allows maximal

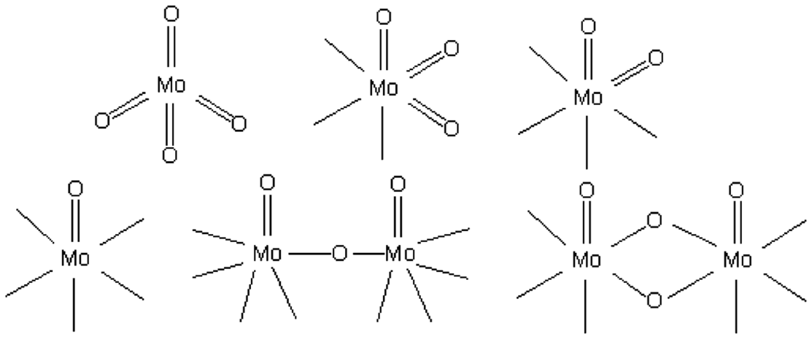


Figure 2. Structures of oxo complexes of molybdenum (VI).

utilization of the *d*-orbitals (*dxz*, *dyz*, *dxy* with ligands along *x*, *y*, and *z* axes) of the acceptor by strong-donor oxo-groups (16). Many authors (16–19) note structural fragment characteristics of Mo(VI) complexes: *cis*-MoO_2^{2+} and *fac*-MoO_3 for mononuclear complexes and $Mo_2O_3^{6+}$ and $Mo_2O_5^{2+}$ for binuclear complexes. The molybdate ion MoO_4^{2-} containing four terminal oxygens prevail in solutions at pH > 7 and have a tetrahedral configuration. With a decrease in pH, the coordination number increases from 4 to 6, and octahedral Mo(VI) complexes start to prevail in the solution (16). Analysis of the thermodynamic characteristics of reactions of successive protonation of the molybdate ion showed (20) that the coordination number changes in going from the monoprotonated molybdate ion $HMoO_4^-$ having the tetrahedral structure to the diprotonated octahedral species $[MoO_2(OH)_2(H_2O)_2]$. At the same time, the tendency toward formation of polynuclear compounds becomes considerably weaker with decreasing pH. A schematic diagram of Mo(VI) oxo-species in aqueous solution is displayed in Fig. 3. As the acid concentration is increased, the dioxomolybdenum ion $[MoO_2(OH)(H_2O)_3]^+$ is formed by a protonation reaction (Eq. 1):

$$\begin{aligned} &pH \leq 2\ [MoO_2(OH)_2(H_2O)_3] \\ &pH < 1 : [MoO_2(OH)_2(H_2O)_2] + H^+ \Longleftrightarrow [MoO_2(OH)(H_2O)_3]^+ \end{aligned} \qquad (1)$$

The equilibrium constant of this reaction (1), $K_{eq} = 11.4$ in 2 M $HClO_4$, suggests that, without complexing agents, the $[MoO_2(OH)(H_2O)_3]^+$ cation will be the major (>90%) molybdenum species at pH = 0; this

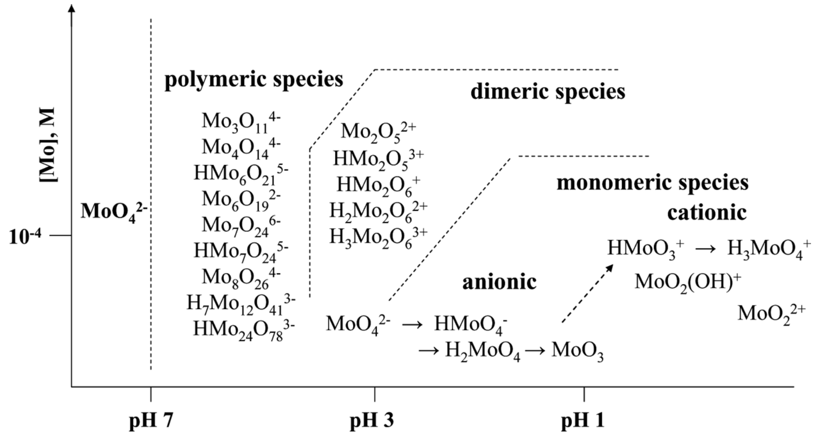


Figure 3. Schematic diagram of Mo(VI) speciation in aqueous phase as an function of pH.

ion contains the stable structural fragment *cis*-MoO_2^{2+}characteristic (19) of mononuclear Mo(VI) complexes. Irrespective of the nature of other ligands, these complexes contain two short Mo = O bonds in the *cis* position. Presumably the much smaller size of the central atom leads to rapid hydrolysis even in acid solutions, and unlike the uranyl ions the molybdenyl ions cannot be studied as free aqueous ions (21). In particular, an increase in the HCl concentration in a solution containing Mo(VI) complexes leads to the formation of chloro complexes in which the MoO_2^{2+} fragment is preserved throughout the acid concentration range (Eqs. 2–4):

$$[MoO_2(OH)(H_2O)_3]^+ + Cl^- \Longleftrightarrow [MoO_2(OH)Cl(H_2O)_2] \tag{2}$$

$$[MoO_2(OH)Cl(H_2O)_2] + Cl^- + H^+ \Longleftrightarrow [MoO_2Cl_2] + 3H_2O \tag{3}$$

$$[MoO_2Cl_2] + Cl^- \Longleftrightarrow [MoO_2Cl_3]^- \tag{4}$$

The reported values of equilibrium constants for molybdenum complexation reactions (Eqs. 2–4) with chloride ($\log K_2 = 0.89$, $\log K_3 = 1.42$, and $\log K_4 = 2.64$) suggest that the prevailing mononuclear Mo(VI) species in HCl solutions are dioxomolybdenum hydroxide (molybdenyl hydroxide) $[MoO_2(OH)(H_2O)_3]^+$ and dioxomolybdenum dichloride (molybdenyl dichloride) $[MoO_2Cl_2]$ (14). Vibrational spectroscopic data confirm the dioxodichlorocomplex $MoO_2Cl_2(H_2O)_2$ as the predominant Mo[VI] species in hydrochloric acid solutions (14); however, in less acidic solutions, even at low Mo(VI) concentrations, bi- and trinuclear complexes cannot be fully excluded from consideration.

Molybdenum (VI) Extraction

In alkaline conditions, the molybdate species are predominant even at higher concentration of Mo, while at lower pH, a variety of polymeric, anionic, neutral and cationic species (22) can occur in the solution (Fig. 3). Their presence and concentration affect the speciation of Mo(VI) and complicate the extraction behavior of molybdenum. Formation of molybdenum dimers in acidic conditions has been studied extensively mainly in perchloric media (23,24) and it was found that increasing the concentration of $HClO_4$ favors the formation of dimers. On the other hand, presence of complexing mineral acids such as HCl, H_2SO_4 and HNO_3 significantly suppresses formation of Mo-dimers; however, at higher Mo concentrations and a lower concentration of complexing acids some dimerization of molybdenum can occur. Monomers of anionic species of Mo(VI) do not complex anions, while cationic species do.

Using symbols $X = Cl^-$, NO_3^-; L = AHA, these formulas can describe speciation of molybdenum in studied aquoes solutions: $[HMoO_3(X; L)]$, $[H_3MoO_4(X; L)]$; $[MoO_2(X; L)]^+$ $[MoO_2(X; L)_2]$; $[MoO_2(X)_3]^-$.

The effect of the metal concentration was investigated and data are summarized in Table 1. Extraction yields of metal were approximately constant in the range of metal concentrations of $10^{-3}-10^{-4}$ M; about 32% was measured for 1 M and 99% for 5 M hydrochloric acid. A decrease in extraction was observed only in 1 M HCl as the metal concentration increased to 0.02 mol/L, probably due to the polymerization of molybdenum that occurs rather at a lower concentration of complexing acid. For all other studied concentrations of metal, either no dimerization of Mo occurs, or if does, it does not have any significant effect on molybdenum extraction. Therefore, $[Mo(VI)] = 1 \times 10^{-3}$ M was chosen as a constant metal concentration for all extraction studies in this investigation.

The dependences of distribution ratios of molybdenum on molar activity of acids in the aqueous phase are displayed in Fig. 4 (white symbols). Activities of nitric and hydrochloric acids were adopted from SIT Database (Specific Ion Interaction Theory Database by IUPAC, published elsewhere). In the wide concentration range of HNO_3, the fission products are not extracted by TBP, and the distribution ratios of molybdenum in nitrate system is very low (< 0.01). From the other side, significantly higher extraction yields of Mo(VI) were observed for HCl/TBP (Fig. 4a) and HNO_3/CMPO/TBP systems (Fig. 4b). Much better extraction of molybdenum with TBP in chloride system can be explained by a stronger complexation affinity of chloride anion to cationic species of Mo (25). Then the extraction process involves this reaction:

$$\begin{aligned} &MoO_2(OH)Cl(H_2O)_2 + Cl^- + H^+ \\ &\quad + 2TBP \Longleftrightarrow [MoO_2Cl_2 \cdot TBP_2] + 3H_2O \end{aligned} \tag{5}$$

Table 1. Extraction of molybdenum as a function of its concentration in the initial aqueous phase

	Extraction yields (%)	
Mo [mol.dm^{-3}]	1 M HCl	5 M HCl
2.67×10^{-4}	32.8	99.4
6.15×10^{-4}	31.5	99.4
1.07×10^{-3}	31.4	99.4
1.60×10^{-3}	31.0	99.0
6.42×10^{-3}	34.1	99.2
2.14×10^{-2}	22.4	99.2

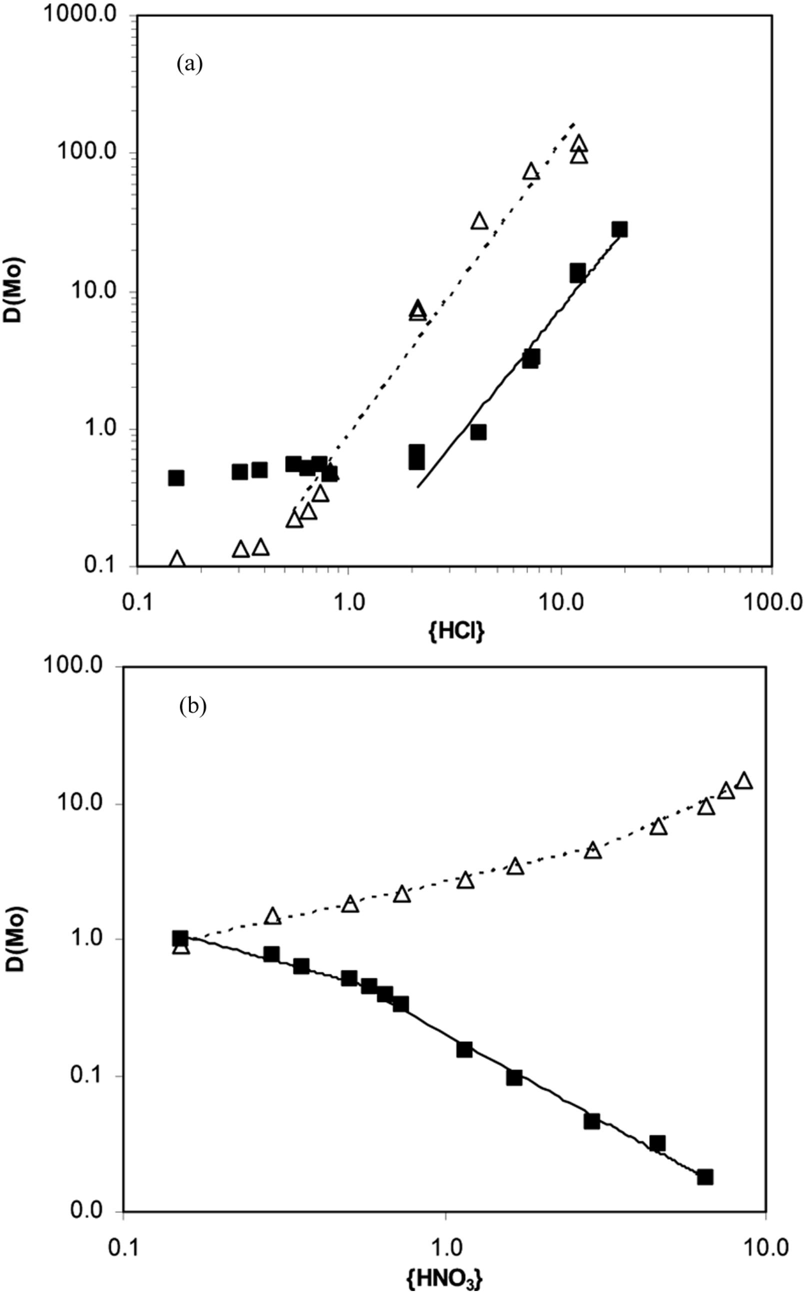


Figure 4. Distribution ratio of Mo(VI) (1.07×10^{-3} M) as a function of aqueous activity of acid: HCl/TBP (a), HNO_3/CMPO/TBP (b); no AHA (Δ); 0.4 M AHA (■).

At lower concentrations of HCl a weak extraction of H_2MoO_4 and $HMoO_3Cl$ molybdenum species is expected, while at $HCl > 1M$, MoO_2Cl_2 are the extracted species. Solvation number 2 for both the chloride and TBP was confirmed by the slope analysis of the plots of log D vs. log {HCl} and log [TBP].

Larger extraction yields of molybdenum from nitric acid solutions with the TRUEX solvent (Fig. 4b, white symbols) than with PUREX solvent can be explained by the intramolecular buffering effect of CMPO. CMPO is a bifunctional neutral ligand that contains both the phosphoryl and carbamoyl group. In the acidic solutions, the phosphoryl groups coordinate to the metal ions, while the carbamoyl groups are considered to be protonated. The protonated carbonyl group should act as a shield against incoming acid through electrostatic interactions (26). By this effect, the distribution ratio of metal in the TRUEX solvent extraction is less affected by the extraction of nitric acid. Besides, the carbamoyl groups are considered to coordinate with the metal ions with an increase of ionic strength. Depending on the acid concentration, different slopes of log-log plots are measured which indicates that different species are extracted. The MoO_2^{2+} species (8,9) are predominant at higher HNO_3 concentration ($>2M$), in lower range of HNO_3 (0.2–2 M), anionic species such as $HMoO_4^-$ and cationic species as $HMoO_3^+$ can be present in the solutions (8). It was proposed (7) that CMPO dioxomolybdenum (molybdenyl) is extracted with TRUEX solvent as an adduct with 2 molecules of CMPO (slope = 2 in log-log plot) and 1 or 2 molecules of nitrate:

$$HMoO_3^+ + NO_3^- + 2CMPO \Longleftrightarrow HMoO_3(NO_3).(CMPO)_2 \qquad (6)$$

$$H_3MoO_4^+ + NO_3^- + 2CMPO \Longleftrightarrow H_3MoO_4(NO_3).(CMPO)_2 \qquad (7)$$

At lower HNO_3 concentration also $HMoO_4^-$ species can be present in solution and extracted as neutral H_2MoO_4. In more acidic media, 2 molecules of nitrate can be co-extracted:

$$MoO_2^{2+} + 2NO_3^- + 2CMPO \Longleftrightarrow MoO_2(NO_3)_2.(CMPO)_2 \qquad (8)$$

$$H_2MoO_3^{2+} + 2NO_3^- + 2CMPO \Longleftrightarrow H_2MoO_3(NO_3)_2.(CMPO)_2 \qquad (9)$$

However, we did not observed slope = 2 in the log-log plot of measured data. Experimental results gave a straight line with slope of $n = 0.5$ for $HNO_3 < 2\,M$ and $n = 1$ for concentrations higher than 2 M. Smaller slopes suggest that at least two species are extracted from solution (with and without nitrate in molecule), even though we found that Beer Law is valid in the studied region of metal concentration.

Effect of Acetohydroxamic Acid on Distribution of Molybdenum (VI)

Addition of AHA changes the distribution ratio of molybdenum significantly in both the chloride and nitrate extraction systems. The dependences of D_{Mo} on the molar activities of acids in the presence of 0.4 M AHA are shown in Fig. 4 (dark symbols).

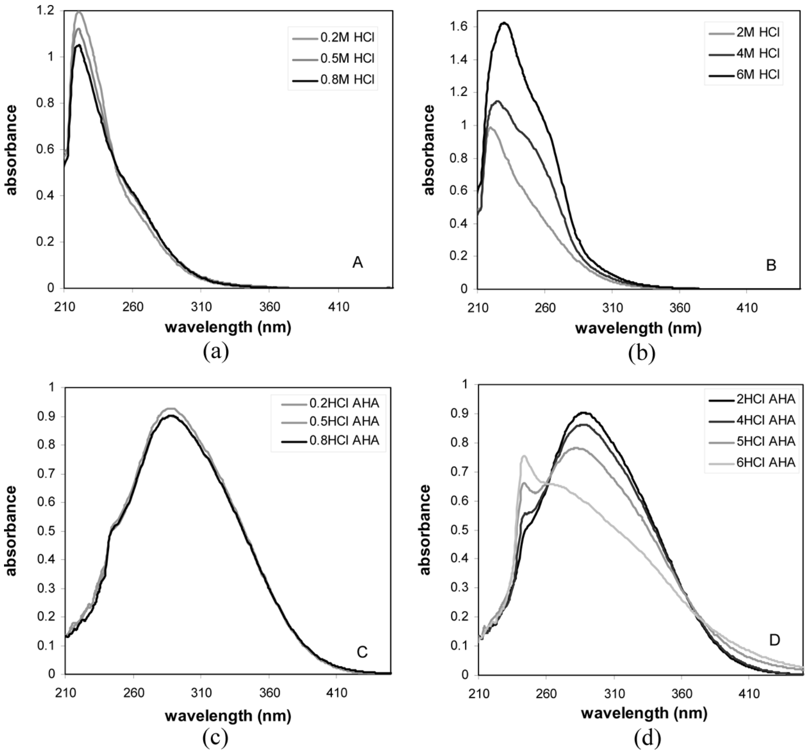
Very interesting behavior of molybdenum at $HCl < 1\,M$ was observed when AHA was added into aqueous phase. In general, because of the high pK_a value of acetohydroxamic acid (9.02) (27), metal ions are more likely complexed with AHA at low acidity. The presence of AHA significantly increased the extraction of molybdenum in this region which can be explained by a shift in molybdenum speciation toward extractable cationic species. This region is characterized by a practically constant D; see the zero slope in the log-log plot of D vs. activity of HCl in Fig. 4a. For higher concentrations of HCl the distribution ratio of Mo continuously increases, creating a parallel slope $n = 2$ in the log-log plot of D vs. $\{HCl\}$. These results suggest that complexation between molybdenum cationic species and AHA is suppressed in high HCl concentration due to formation of MoO_2Cl_2 species.

An absolutely different dependence was observed when AHA was added to the HNO_3/CMPO/TBP extraction system. In the presence of AHA, D(Mo) were gradually decreasing with an increase of nitric acid concentration in aqueous phase. It indicates that the hydroxamate group forces the changes in coordination with Mo(VI) toward molybdenyl hydroxamate species. The complexes of MoO_2^{2+} with AHA are formed even in the region of high acid concentration, and are responsible for the gradual decrease observed in the distribution ratios of Mo in the nitrate/CMPO system. Furthermore, it can be assumed that in the region of lower HNO_3 concentration, the presence of anionic species is more auspicious, and therefore, the complexation of Mo with AHA is more suppressed.

Speciation of Mo(VI) in Aqueous Phase by Absorption Spectroscopy

Chloride System

Formation of different molybdenum species in the nitrate and chloride matrices for different acid concentrations was confirmed also by UV spectroscopy. Several representative spectra recorded on the Mo(VI)-HCl-AHA and Mo(VI)-HNO_3-AHA systems are shown in Figs. 5, 6. Increase of HCl concentration from 0.2 M to 2 M caused decrease of absorbance of Mo(VI) at 220 nm due to a shift in speciation of metal



(a) (b)

(c) (d)

Figure 5. Absorption spectra of molybdenum(VI) ($[\mathrm{Mo}] = 3.15 \times 10^{-4}\,\mathrm{M}$) at small (a) and large (b) concentration of HCl and 0.4 M AHA (c, d).

from anionic $\mathrm{HMoO_4^-}$ to cationic $\mathrm{HMoO_3^+}$ species which have lower extinction coefficient at 220 nm (Fig. 5a). With further increase of HCl concentration, the spectra of molybdenum change significantly, because of the predominance of molybdenyl-chloride complex species at higher HCl concentration in aqueous solution. These changes can be seen also from rising of absorbance for shoulder of $\mathrm{MoO_2^{2+}}$ at region of 250–260 nm that is characteristic for molybdenyl chloride species (28) (Fig. 5b). Addition of AHA to the HCl system changed the shape of molybdenum spectra dramatically and formation of molybdenum-AHA complex in the aqueous solution with maximum absorbance at 280–290 nm was observed (Fig. 5c). Upon addition of AHA into aqueous solution presence of anionic species is negligible due to the formation of $\mathrm{HMoO_3^+}$ and $\mathrm{MoO_2^{2+}}$ species which are complexed by chloride and hydroxamic acid (Fig. 5c). Although hydrochloric acid at a concentration lower than 2 M does not have any significant effect on the formation of Mo-AHA

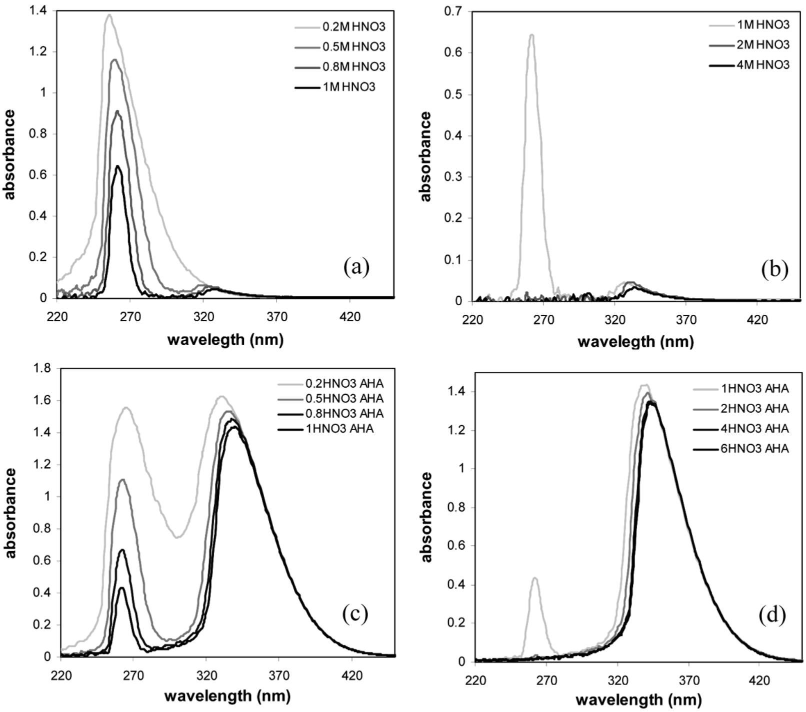


Figure 6. Absorption spectra of molybdenum(VI) ($[Mo] = 1.05 \times 10^{-3}$ M) at small (a) and large (b) concentration of HNO_3 and 0.4 M AHA (c, d).

complex (at short contact time, hydrolysis of AHA is negligible), a higher concentration of HCl decreases the complexation between AHA and molybdenum (Fig. 5d), which is in good accordance with data from extraction experiments (Fig. 4).

Nitrate system

The molybdenum spectra at lower nitric acid concentrations have a characteristic shape with two clearly distinguished peaks. The peak at 250–260 nm region belongs to anionic molybdenum species of $HMoO_4^-$ and cationic $HMoO_3^+$, respectively, while the small peak beyond 300 nm belongs to molybdenyl species which are probably just partially complexed with nitrate (Fig. 6a, b). The changes in the ultraviolet region of spectra are apparently due to the formation of cationic species with an increase of the nitric acid concentration from 0.1 M to 2 M. The absorption peak at region of 250–260 nm first decreased and then disappeared completely in 2 M HNO_3 (Fig. 6b). These data correspond very well with the data acquired in the extraction experiments, and confirms that anionic molybdate species are present in the lower concentrations of acid only, while at larger concentration of acid, cationic species are predominant. Under studied acidic conditions, the ligand, acetohydroxamic acid, is not dissociated (HL = HAHA, L = AHA^{-1}), so the following complexation and proton-consuming processes occur:

$$MoO_4^{2-} + HAHA + 2H^+ \Longleftrightarrow [HMoO_3(AHA)] + H_2O \qquad (10)$$

$$[HMoO_3(AHA)] + HAHA \Longleftrightarrow [MoO_2(AHA)_2] + H_2O \qquad (11)$$

$$[HMoO_3(AHA)] + HNO_3 \Longleftrightarrow [MoO_2(AHA)(NO_3)] + H_2O \qquad (12)$$

In the presence of AHA in Mo/HNO_3 system, an intensive hyperchromic shift was observed in the spectrum region above wavelength of 300 nm (Fig. 6c). Changes of spectra in the region of 250–260 nm of the Mo(VI) spectrum in HNO_3 are weak, but a partial decrease of absorbance in this region can be probably explained by a shift in speciation toward $HMoO_3^+$ and MoO_2^{2+} species upon addition of AHA. A sharp rise of absorbance in the spectrum region of 320–340 nm is explained by complexation of cationic molybdenyl species with acetohydroxamic acid and higher absorption coefficient. Data from absorption spectroscopy also confirm that the formation of Mo-AHA complex occurs even in 6 M nitric acid (Fig. 6d).

Molybdenum Species in the Extraction Organic Phase

It is of a great importance, scientific and technological, to look onto speciation of extracted metal in the organic phase. The distribution ratio of molybdenum was found much higher after addition of acetohydroxamic acid (0.4 M) to aqueous phase containing HCl with a concentration below 1 M. Absorption spectra of Mo(VI) in TBP phase after extraction from HCl solution (Fig. 7a) showed a significantly higher absorbance for system when AHA was present in aqueous phase. Occurrence of a peak at 230 nm after extraction from 0.2 M HCl and 0.4 M AHA leads to the conclusion that extraction of molybdenum is enhanced due to complexation with chloride (Fig. 7a). On the other hand, presence of the second wide peak with a maximum at 280 nm also suggests that molybdenum species associated with hydroxamate are present in the organic phase. Presence of molybdenum-hydroxamate species in the extraction organic phase significantly increases the absorbance of molybdenum in TBP, which can also be clearly seen from the spectrum of Mo in TBP after extraction

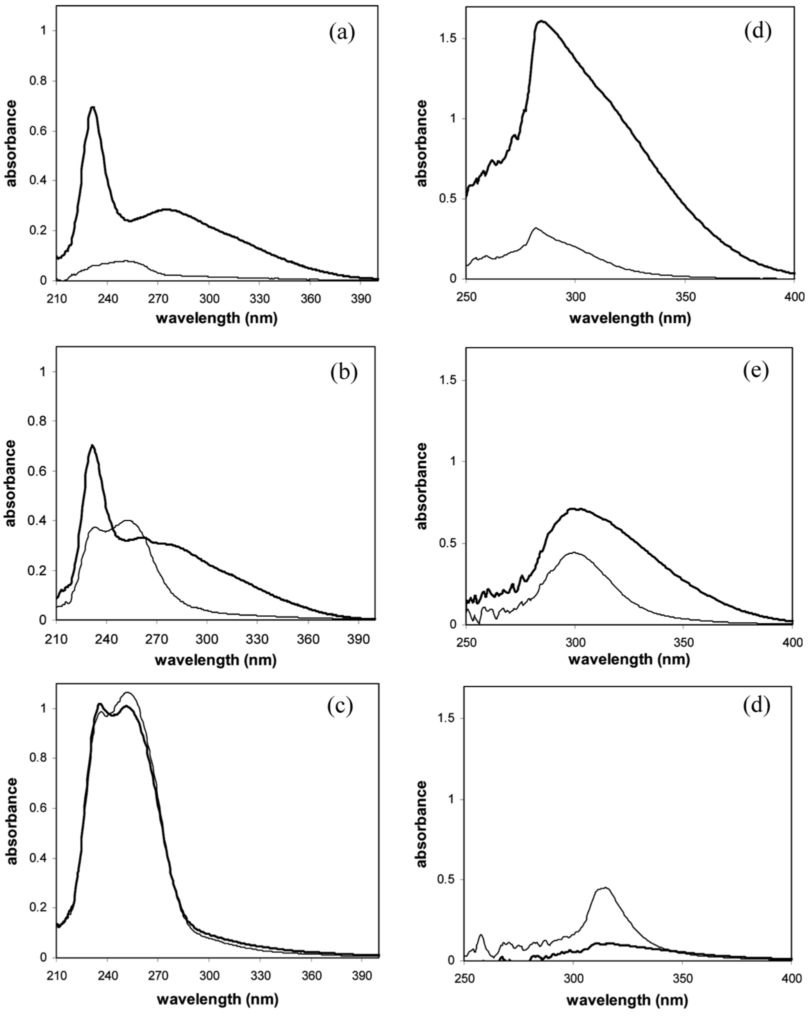


Figure 7. Spectra of Mo(VI) in the extraction organic phase of TBP/HCl (a–c) and CMPO/TBP/HNO_3 (d–f) after extraction from 0.2, 1 and 6 M HCl or HNO_3 in the absence (thin line) and presence of AHA (0.4 M, bold line) in the initial aqueous phase.

from 1 M HCl and 0.4 M AHA (Fig. 7a,b). High concentration of HCl ($\geq$6 M) suppresses formation of Mo-AHA species in water; however, it doesn't lead to a significant increase of the molybdenum extraction (Eq. 4), and the absorbances of organic phase agitated with and without AHA are practically the same (Fig. 7c).

Different shapes of molybdenum spectra in the TRUEX organic phase agitated with 0.2, 1, and 6 M HNO_3 without AHA (Fig. 7d–f, thin lines) confirm extraction of at least two different species of Mo(VI). While at 0.2 M HNO_3 the extracted species are non-nitrate species with characteristic absorption maximum at 270–280 nm, at higher nitric acid concentration the molybdenyl nitrate species causing a shift of the absorbance maximum to 290–330 nm are predominant. When AHA was added to low concentrations of HNO_3 similar results, like for the TBP/HCl system were obtained: the Mo spectra of the TRUEX organic phase agitated with 0.4 M AHA in 0.2 and 1 M HNO_3 (Fig. 7d,e) had a higher absorbance than without AHA. Spectroscopic analysis of extraction samples with higher concentrations of HNO_3 confirmed decreased values of D(Mo) (Fig. 4b) and formation of non-extractable molybdenyl-hydroxamate-nitrate species when AHA is added.

Co-extraction of ternary metal-AHA-nitrate complexes with neutral organophosphorous extractants formed at lower concentrations of nitric acid was also reported earlier for extraction of U(VI) (29,30) and Pu(IV) (31,32) with tributyl phosphate from nitric acid solutions in the presence of AHA. However, while formation of Mo(VI)-AHA and Pu(IV)-AHA (31,32) complexes in the extraction organic phase was identified immediately after extraction, U(VI)-AHA (29,30) species was observed only after prolonged contact of aqueous and organic phase. Besides other factors, this difference can be explained by the strength of hydroxamate complexes with studied metals. From stability constants determined from pH-metric and spectrophotometric data, $\log\beta_1 = 8.22$ for $[U(VI)(AHA)]^+$ (27), 14.2 for $[Pu(AHA)]^{3+}$ (27) and 17.16 for $[HMoO_3AHA]$, (33) and $\log\beta_2 = 15.3$ for U(VI) $(AHA)_2$, (27) 24.1 for $[Pu(AHA)_2]^{2+}$ (27) and 32.46 for $[MoO_2AHA_2]$, (33) it is evident that both plutonium(IV) and dioxomolybdenum(VI) have much larger affinity toward hydroxamate than uranium(VI); therefore, in the case of such strong extraction solvents as CMPO or TBP, a significant fraction of their ternary hydroxamate complexes with nitrate or chloride will be also co-extracted.

CONCLUSIONS

The extraction and spectrophotometric experiments of Mo in the TBP/HCl and CMPO/HNO_3 systems were performed. Different molybdenum species are extracted by TBP and CMPO from lower and higher concentrations of HCl and HNO_3, respectively. At lower acid concentration, the molybdenum species as $HMoO_4^-$, $HMoO_3^+$ are present in the solution, while at higher acid concentration MoO_2^{2+} are predominant.

Upon addition of AHA to 0.2–1 M HCl, increased distribution ratios of molybdenum were caused by a shift in Mo speciation toward extractable cationic species. For all others conditions, D_{Mo} was suppressed by the presence of AHA. Extraction yields of molybdenum for CMPO/HNO_3/AHA system decrease with increased concentration of nitric acid due to predominance of molybdenyl-hydroxamate species in the aqueous phase; however, molybdenyl-hydroxamate complex species penetrate into the organic phase. The presence of molybdenum-AHA species in both the TBP and CMPO extraction organic phases was identified by absorption spectroscopy despite that the distribution ratio of molybdenum is markedly low. Higher absorbencies and low distribution ratios measured for the same organic phase might be explained only by a much higher extinction coefficient of solvate adducts of molybdenyl-hydroxamate with TBP (CMPO).

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