Speciation of Molybdenum(VI) in Chloride Media at Elevated Mo Concentrations

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ABSTRACT: Speciation of Mo(VI) in chloride media (0.5−11 M HCl) at elevated Mo concentrations (0.1−300 mM Mo) was investigated using UV spectroscopy. In addition to five major monomeric species, H₂MoO₄, H₃MoO₄⁺, H₃MoO₄Cl, MoO₂Cl₂, and MoO₂Cl₃⁻, chemometric analysis of UV spectra suggests the presence of three cationic dinuclear species that predominate in solutions of 1−4.5 M HCl at >20 mM Mo concentrations. Thermodynamic values and molar absorptivity spectra were calculated from UV spectrophotometric data using refined numerical methods. The stability constants determined for three Mo dimers are log β = 3.53 ± 0.05 (H₂Mo₂O₅²⁺), log β = 3.60 ± 0.04 (H₃Mo₂O₅³⁺), and log β = 2.91 ± 0.03 (H₃Mo₂O₆Cl₂⁺).

INTRODUCTION

The radionuclide ⁹⁹ᵐTc is used in approximately 80% of all nuclear medicine procedures performed worldwide.¹ The short half-life of the metastable ⁹⁹ᵐTc (6.0 h) precludes its chemical separation at the production site. Instead, the longer-lived parent ⁹⁹Mo (66 h half-life) is sent to radiopharmacies, where the grown-in ⁹⁹ᵐTc is separated from Mo and used immediately for diagnostics. Traditionally, production of ⁹⁹Mo was obtained through the fissioning of >90% high-enriched uranium (HEU) targets. A shift in U.S. policy occurred with the 2011 American Medical Isotopes Production Act, which was aimed at establishing a reliable domestic supply of ⁹⁹Mo while eliminating the use of HEU in the various medical isotope supply chains.²,³ In accordance with these goals and those put forth by the International Atomic Energy Agency, most manufacturers of fission-made ⁹⁹Mo have converted research reactors and medical isotope production facilities worldwide to less proliferation-sensitive low-enriched uranium (<20%²³⁵U) sources.⁴ However, several novel nonuranium alternatives for producing ⁹⁹Mo are also gaining attention, such as accelerator-based production via the bremsstrahlung photoneutron reaction ¹⁰⁰Mo(γ,n)⁹⁹Mo or use of neutron capture ⁹⁹Mo(n,γ)⁹⁹Mo. In both cases, enriched ¹⁰⁰Mo or ⁹⁹Mo is often required to produce significant activities of ⁹⁹Mo economically. Because of the high cost of enriched material ($500−1000/g for kilogram quantities), efficient recycling strategies for Mo must be developed.

The recycling of enriched Mo into fresh target material involves the conversion of aqueous Mo(VI) solutions, typically in alkaline media (e.g., KOH, NaOH), to Mo(0) metal powders. Important qualities of a recycle process include high recovery yields, high throughput, meeting purity specifications, and obtaining recycled target characteristics similar to those of the original material. The Mo solvent extraction (MOEX) process has recently been proposed as a viable option for recycling enriched Mo material.⁵ The MOEX system relies on extraction of high concentrations of Mo (~0.3 M) in HCl by tri-n-butyl phosphate (TBP) to achieve decontamination from Na, K, and other impurities. However, there is limited understanding of the aqueous Mo chemistry occurring in this system. Recent investigations indicate that the Mo species primarily extracted by TBP is the dichloromolybdenyl species MoO₂Cl₂, occurring as an adduct with two TBP molecules.⁶ However, insight into Mo(VI) polyoxometalate chemistry that will be discussed in this paper suggests that polynuclear complexes constitute a significant fraction of aqueous Mo species when it is present at higher concentrations.

The diversity of mono- and polynuclear Mo species existing simultaneously in acid solutions poses a great challenge to understanding and predicting their aqueous distribution at high Mo concentrations. The simple tetrahedral molybdate ion MoO₄²⁻ is the well-known dominant species in alkaline solutions. Mononuclear forms of Mo(VI) predominate when Mo concentrations are low (<0.1 mM), following a series of

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protonation steps and complexation with chlorides beginning with protonation of molybdate near pH 7

\[
\text{MoO}_4^{2-} + H^+ \leftrightarrow H\text{MoO}_3^- 
\] (1)

\[
\text{HMoO}_3^- + H^+ \leftrightarrow H_2\text{MoO}_4 
\] (2)

\[
\text{H}_2\text{MoO}_4 + H^+ \leftrightarrow H\text{MoO}_4^+ 
\] (3)

\[
\text{H}_2\text{MoO}_4^+ + Cl^- \leftrightarrow \text{HMO}_4\text{Cl} 
\] (4)

\[
\text{H}_2\text{MO}_4\text{Cl} + H^+ + Cl^- \leftrightarrow \text{MO}_4\text{Cl}_2 + 2\text{H}_2\text{O} 
\] (5)

\[
\text{MO}_4\text{Cl}_2 + Cl^- \leftrightarrow \text{MO}_2\text{Cl}_3^- 
\] (6)

Between pH 0 and 1, the predominant species of Mo(VI) is molybdc acid H$_2$MoO$_4$ and its protonated form, the H$_3$MoO$_4$ cation. In solutions of HCl, the protonated molybdc acid undergoes a rapid, two-step complex formation with a first-order dependence on both [H$^+$] and [Cl$^-$] to form the first chlorinated monomer species, H$_3$MoO$_4$Cl.$^8$ A second chlorination step leads to the formation of the neutral complex MO$_4$Cl$_2$ containing the molybdyl [MoO$_2$]$^{2+}$ moiety, which then predominates throughout acid concentrations >5 M in coordination with chloride ions.

There is a favorable enthalpy change ($\Delta H = -47$ kJ/mol) for the MO$_4$$^{2-}$/HMOO$_3^-$/H$_2$MoO$_4$ reaction owing to the bond energy gained from an increase in coordination number upon protonation of molybdate.$^9$ As such, the changes in formulation from four-coordinate MO$_4^{2-}$ to six-coordinate MoO(OH)$_5^-$ and Mo(OH)$_6^-$ are typically used to emphasize the thermodynamic driving forces behind complex formation. The true structure of molybdc acid has been identified by various authors after extensive experimental and DFT analyses as taking the form of the octahedral MO$_4$(H$_2$O)$_3$ complex.$^9,10$ To reduce the confusion that often occurs around hydrated formulations, this paper employs general formulas (e.g., H$_2$MoO$_4$) for all species.

The ability of tetrahedral MO$_4^{2-}$ to expand its coordination sphere from 4 to 6 allows molybdate subunits to condense to various electron-dense isopolymolybdate complexes in weakly acidic media (pH 1 to 5). These arrangements are facilitated by Mo–O π-bonding of MoO$_4$ subunits sharing edges and vertices. Mo–O bond lengths in isopolyanions of Mo are shorter because of π-bonding, resulting in distinct UV spectra compared to dinuclear cations, which contain the σ-bonded Mo–O–Mo bridge. Examples of the isopolyanions of Mo(VI) include [MoO$_4$]$^{2-}$, [Mo$_2$O$_{2+}$]$^{2+}$, [Mo$_6$O$_{12+}$]$^{2-}$, and their protonated variants that form large three-dimensional frameworks whose nuclearity and equilibria have been fairly well characterized.$^7$ Partial reduction of Mo(VI) can lead to covalent self-assembly of Mo into nanosized, mixed-valence Mo$^{VI}$–Mo$^{V}$ entities such as [Mo$_{12}$O$_{24}$H$_4$(H$_2$O)$_{76}$]$^{14-}$. The unique nature and various applications of transition-metal polyoxometalate chemistry have made it a principal focus of aqueous Mo research. In contrast to the tendency of most isopolymolybdate clusters to occur as anions in aqueous solutions, the dinuclear complexes of Mo(VI) are predominantly cationic. One exception is the singly charged HMO$_2$$^{2-}$ anion, whose existence between pH 2 and 6 is so far supported only by quantitative treatment of spectrophotometric evidence.$^{12}$ Dimerization of Mo in noncomplexing acids such as HClO$_4$ is strongly promoted by medium effects, namely, by an increase in ionic strength and decrease in water activity.$^{13}$ In these conditions, Mo condensation can occur at relatively low Mo concentrations (~1 mM) with rapid kinetics.$^{14}$ Previous spectroscopic and calorimetric investigations of Mo(VI) revealed the presence of three oxocation dimers, HMO$_4$$^{2+}$, MoO$_2$$^{2+}$, and HMO$_2$$^{3+}$, which begin to form just above 0.1 mM Mo.$^{12-15}$ The dimerization reaction was shown to be enthalpy-driven ($\Delta H = -30$ kJ/mol), which is derived from the formation of a free water molecule to form MO$_4$$^{2-}$ coupled with an unfavorable entropy change due to an increase in molecular order.$^{16}$ Dimerization of two singly charged monomers (eq 3) results in the doubly charged dimer MO$_4$$^{2+}$ and the following equilibria are considered

\[
2\text{H}_2\text{MoO}_4 + 2\text{H}^+ \leftrightarrow 2\text{H}_2\text{MoO}_4^+ + \text{H}_2\text{O} 
\] (7)

\[
\text{MoO}_4^{2+} + \text{H}_2\text{O} \leftrightarrow \text{MoO}_6^{2+} + \text{H}^+ 
\] (8)

\[
\text{MoO}_4^{2+} + \text{H}^+ \leftrightarrow \text{MoO}_5^{3+} 
\] (9)

The major dimeric species in 1 M HClO$_4$ solutions is the divalent cation MO$_4$$^{2+}$. Dimeric Mo(VI) cations notably show a characteristic peak at ~245 nm, which has been attributed to the unique Mo–O–Mo oxygen bridge joining two octahedral Mo units in the [MoO$_4$]$^{2-}$ moiety. This peak is absent in spectra of isopolyanions, where μ-oxo bridging is not present and bonding is instead composed of edge- and vertex-sharing MO$_4$$^{2-}$. The [MoO$_4$]$^{2-}$ structure has been verified by Raman and EXAFS spectroscopies as a constituent of various cationic dimers having a bond angle of ~125°. Because of the unique bonding nature of the dimeric species, UV spectrophotometry can readily distinguish Mo dimeric cations from their mononuclear or anionic polymeric forms.

Mo(VI) condensation has been observed under strong acid conditions in both complexing (HCl) and noncomplexing (HClO$_4$) media; however, the main body of research has focused almost entirely on the latter.$^7,16$ To the best of our knowledge, the nature of polynuclear Mo(VI) complexes in HCl has hitherto not been identified. It is likely that the formation of dinuclear species would occur in HCl and that additional species complexed with chlorides are also possible. Applying UV spectrophotometric techniques, we have measured the absorption spectra and identified the major Mo(VI) species in 0.5–11 M HCl solutions using refined numerical processing. Stability constants at varying ionic strengths were estimated by accounting for activity coefficients using the modified Bromley theory.$^{19}$ In this work, we seek to identify mono- and polymeric species of Mo present in the aqueous phase during the MOEX solvent extraction process.

## RESULTS AND DISCUSSION

**Mononuclear Mo(VI) Species.** UV spectra of solutions collected from 0.5 to 11 M HCl with 0.1, 2, 20, and 300 mM Mo are shown in Figure 1. At 0.1 mM Mo, the concentrations of Mo(VI) polynuclear species are known to be below 1%. The first step of the analysis was to compare these absorbance spectra to those collected by previous authors who studied the monomeric Mo(VI) system. The 0.1 mM spectra show that a dominant peak with a maximum near 226 nm increases with acid concentration. At high HCl concentrations, a shoulder region forms in the interval of wavelengths between 250 and 270 nm. These spectra show strong agreement with those of previous authors, including the tangential contact of the...
shoulder at 256–274 nm, supporting the conclusion that it
does not constitute an isosbestic region.9,24 The high-HCl
spectra appear nearly identical across all Mo concentrations,
indicating that little to no speciation di-
gerences occur under
these conditions. However, signi-
fi-
cant spectral changes appear
in the less acidic region between approximately 0.5 and 5 M
HCl (brown-black lines in Figure 1) as Mo concentration
increases.

To explore the monomeric equilibrium model, the 0.1 mM
Mo spectra were evaluated using the HypSpec program. A set
of formation constants (log K) for monomeric Mo(VI) species
in chloride media that was determined in a previous work was
supplied to the program as initial estimates: H3MoO4
+ (0.934 ± 0.01), H3MoO4Cl (−0.89 ± 0.04), MoO2Cl2 (−1.40 ± 0.04), and MoO2Cl3
− (−2.64 ± 0.09).8 The comparison
between calculated and experimental spectra resulted in an
excellent fit (σ = 3.6 × 10−3), confirming that the data are
adequately described by monomeric species. Stability constants
(log β) were determined considering H2MoO4 as the starting
Mo species forming complexes with protons and chloride ions.
Formation constants (log K) and log β for all monomeric
species are summarized together with dinuclear species in
Table 1 where they are compared with literature data.

Molar absorptivity spectra for the identified monomeric Mo(VI) species
in HCl determined from 0.1 mM Mo absorbance spectra.

![Figure 1. UV−vis absorption spectra collected for 0.1 (A), 2 (B), 20 (C), and 300 mM (D) Mo in 0.5−5 M HCl (brown-black) and 5.5−11 M HCl (black-blue). Spectra were recorded in quartz cuvettes of path length 10, 1.0, 0.1, and 0.01 mm, respectively.](https://dx.doi.org/10.1021/acsomega.0c02858)

![Figure 2. Molar absorptivity spectra for monomeric Mo(VI) species in HCl determined from 0.1 mM Mo absorbance spectra.](https://dx.doi.org/10.1021/acsomega.0c02858)
The shoulder region at ca. 260–270 nm (Figure 1) is caused by the formation of MoO$_2$Cl$_2$ and MoO$_2$Cl$_3^-$ species (eqs 5 and 6), which show equivalent extinction coefficient values at these wavelengths (Figure 2) and thus their interconversion results in a constant absorbance between 260 and 270 nm.

Discrepancies between experimental stability constants determined here and those from the literature are most likely the result of different assumptions regarding the calculation of activity coefficients. Activities for H$_3$O$^+$ and Cl$^-$ ions, which in this study were obtained by Bromley’s method, differ from literature data mostly at higher acid concentrations where even small changes in activity coefficients lead to more pronounced differences in activities. This conclusion is supported by the observation that stability constants for the lower-acid species, H$_2$MoO$_4^+$, H$_2$MoO$_4$Cl, and MoO$_2$Cl$_2$, are within experimental error, and only the MoO$_2$Cl$_3^-$ formation constant shows a more pronounced difference.

Figure 3 shows the speciation diagram for monomeric Mo species based on experimentally determined stability constants.

![Figure 3. Speciation diagram of monomeric Mo(VI) in 0.5–11 M HCl obtained using stability constants determined in this work.](image)

The diagram confirms that at 0.5 M HCl, the protonation of molybdic acid is already ~80% complete. A concentration of roughly 3.5 M HCl is required for 50% conversion to the MoO$_2$Cl$_2$ species. The maximum abundance of MoO$_2$Cl$_2$ is about 85% and occurs at 5–5.5 M HCl. Then, at HCl concentrations >6 M, the absorbance spectra are satisfactorily described with only the di- and tri-chloro molybdenyl complexes. Similarities observed in absorption spectra at high HCl (>6 M) across all Mo concentrations investigated (Figure 1) indicate that only monomeric MoO$_2$Cl$_2$ and MoO$_2$Cl$_3^-$ species are present. This observation will be further discussed in more detail.

The speciation diagram and individual molar absorptivity spectra calculated from the experimental UV data in this work are nearly identical to those produced in the work of Cruywagen and Rohwer. In particular, molar absorbance spectra for various Mo concentrations (Figure 1) at lower HCl concentrations indicate several changes in spectral features as the Mo concentrations increase. In the 2 and 20 mM Mo spectra, significant deviations from monomeric spectra occur below 5 M HCl (brown lines). This observation correlates well with the expectation for Mo dimerization, which was previously confirmed in this region in noncomplexing HClO$_4$ media.

Spectra collected across the Mo concentration range from 2 to 300 mM were added to the 0.1 mM Mo analysis and evaluated for their fit to the monomeric model. As expected, the poor fit obtained indicates that the presence of only monomeric Mo species at 0.1 mM Mo does not sufficiently describe the absorbance spectra at higher Mo concentrations. Evidence for this was also observed by Cruywagen at Mo concentrations greater than 0.1 mM, where the extinction of Mo(VI) solutions began to deviate from Beer’s law. Therefore, addition of dimeric Mo species needs to be considered to properly analyze spectra at >0.1 mM Mo concentrations.

Individual spectral features of 300 mM Mo in 1.0 M HCl were identified using Gaussian peak-fitting to determine peak positions and intensities. The results are compared with 0.1 mM Mo spectra and displayed in Figure 4, showing that the 300 mM Mo absorbance spectrum can be described as the sum of three peaks at 210, 245, and 274 nm (R$^2$ = 0.99999). The absorption peaks near 210 nm are a common feature of many aquaeous Mo species, as is apparent from the molar absorptivity spectra. Previous literature utilizing molecular orbital calculations have ascribed the absorbance peaks between roughly 200 and 240 nm to ligand-to-metal charge-transfer transitions (O$^{2–}$ → Mo$^{VI}$) from terminal oxygen atoms. At 0.1 mM Mo, absorbance at 210 nm is primarily governed by the monomeric equilibria involving H$_2$MoO$_4^+$ (eqs 2–4), which is the dominant species between 0.5 and 3 M HCl (Figure 2). As Mo concentration increases, the growth of the absorption band at 245 nm indicates that the polynuclear equilibria are increasingly important. As previously stated, it is well documented that Mo dimers contain the μ-oxo bridge (Mo–O–Mo) responsible for the characteristic absorption feature at 245 nm. The formation of this peak in Mo spectra shows that Mo–O–Mo bridging occurs in solutions with ≥2 mM Mo.
This finding strongly suggests that the changes in the absorption spectra at high Mo concentrations are most likely due to formation of cationic dimers.

To gain insight into the number of dimers that may be present, factor analysis via singular value decomposition was performed on the absorbance data. This analysis was applied to all three datasets, that is, 2, 20, and 300 mM Mo (≈20 spectra at each Mo concentration) and on the 0.1 mM Mo and 20 mM Mo datasets separately. The goal of this analysis was to identify the number of major absorbing species contributing to the overall absorbance. The number of significant eigenvalues obtained from 0.1 mM Mo spectra indicates the presence of five species, which is consistent with the monomeric model previously determined. The ≥2 mM Mo data revealed the presence of up to eight factors from these datasets. This result suggests that three new species are forming between 0.1 and 2 mM Mo.

Three known dimeric species could be expected in HCl on the basis of previous investigations in perchloric acid (eqs 7–9): HMo2O6 2+, Mo2O5 2+, and HMo2O5 3+. However, the ionization constant of the singly protonated form HMo2O6 2+ is predicted to be too low for it to occur in significant concentrations under these conditions. The presence of a third dimeric species revealed by factor analysis could be explained by the presence of chlorinated Mo dimeric species. To explore these proposed scenarios, 2 and 20 mM Mo datasets were analyzed by the HypSpec program. Models incorporating known dimeric HMo2O6 2+, Mo2O5 2+, and HMo2O5 3+ species were first examined. Indeed, the exclusion of the singly charged dimer was supported after it showed a poor fit to the data in all models. In this study, an allowance was made for various protonation and chlorination states of dimeric species, tentatively formulated as HmMo2O5Cl2+(2m+n)+ and these were evaluated for their fit to spectrophotometric data. Results from these various models indicate that in addition to two oxocation dimers previously reported in HClO4, it was necessary to include a chlorinated dimer with the formula HMo2O5Cl2+ to explain all absorbing features in the UV spectra. Incorporating the presence of all three dimers, Mo2O5 2+, HMo2O5 3+, and HMo2O5Cl2+, into the HypSpec model with all previously determined monomeric species provided an excellent fit to experimental data. Numerical refinement converged with σ = 9.3 × 10^-3 for all spectra between 0.1 and 20 mM Mo. The model was then applied to treat the 300 mM Mo spectra, with which it provided excellent agreement.

Equilibria and constants for dimeric complexes that were determined by analysis of UV spectra are listed together with the number of major absorbing species contributing to the overall absorbance. The number of significant eigenvalues obtained from 0.1 mM Mo spectra indicates the presence of five species, which is consistent with the monomeric model previously determined. The ≥2 mM Mo data revealed the presence of up to eight factors from these datasets. This result suggests that three new species are forming between 0.1 and 2 mM Mo.

Dependence on Chloride Concentration. The proposed dimeric Mo species were further validated by analysis of 20 mM Mo spectra at 1 M HCl concentration and varying total chloride concentrations (achieved by adding NaCl). From the trends in the speciation diagram of dimeric Mo species (Figure 5), it is apparent that at 1.0 M HCl, all three postulated dimeric Mo species will coexist. The collected absorbance spectra for 20 mM Mo in 1 M HCl and total chloride concentrations of 1−5 M are presented in Figure 7. The overall trend is an increase in absorbance with increasing NaCl concentration at nearly all wavelengths. This result contrasts...
with spectra of increasing HCl concentration, where an isosbestic point occurs at ca. 240 nm (Figure 1C,D). The broad peak developing at ~230 nm resembles spectra of 20 mM Mo obtained at 3–4 M HCl where there are six major species present: \( H_2MoO_4^{+}, \) \( H_2MoO_4Cl^−, \) \( MoO_2Cl^−, \) \( MoO_2^−, \) \( HMoO_2Cl^2+ \), and \( HMoO_2^3− \). The overall increase in absorbance indicates that the concentration of dimeric species is greater at 1 M HCl and 4 M NaCl than at 5 M HCl. However, owing to the presence of many species in this region, the characteristic spectral feature for the Mo dimer at 245 nm is obscured, so analysis of spectra was performed using the equilibrium modeling software. HypSpec analysis of 20 mM Mo spectra in 1 M HCl and varying NaCl concentrations is obscured, so analysis of spectra was performed using the characteristic spectral feature for the Mo dimer at 245 nm when the increase in abundance of chlorinated dimers with higher molar absorptivity in the 220–230 nm range is greater at 1 M HCl and 4 M NaCl than at 5 M HCl.

Equilibrium modeling and factor analysis revealed three major dimeric species present in HCl, doubly and triply charged \( MoO_2^{2+} \) and \( MoO_2^3+ \) cations stable at lower (<4 M) HCl concentrations, and a singly chlorinated dinuclear cation \( HMoO_2Cl^2+ \) which is present in a relevant concentration even at 6 M HCl at 300 mM Mo. It was also demonstrated that for MOEX-relevant conditions at 300 mM Mo and 5 M HCl, about 40% of Mo atoms in the aqueous phase exist in dinuclear form. This, however, does not affect the recovery yields in the MOEX recycle process.

### Experimental Section

Unless otherwise indicated, chemicals were obtained from Thermo Fisher Scientific. Trace metal grade HCl and 18 M \( \text{H}_2\text{O} \) (MilliQ) were used to prepare solutions. A series of Mo stocks were prepared from MoO\(_2\)Cl\(_2\) (Sigma-Aldrich) in volumetric flasks. Mo samples were prepared in batch experiments by mixing stocks to achieve the desired HCl concentration (0.5–11 M HCl). Samples were prepared over a wide range of Mo concentrations (0.1–300 mM Mo). NaCl was used in experiments where it was desired to maintain acid concentration but increase [Cl\(^–\)]. Concentrations of Mo and Na were determined via inductively coupled plasma mass spectroscopy (ICP−MS). Hydrogen ion concentrations of all samples were determined through triple titration with a standardized solution of NaOH. In the calculation of total proton concentrations, an allowance was made for the conversion of molybdenyl to molybdate upon neutralization to pH 7.

\[
\text{MoO}_3^{2+} + 2\text{H}_2\text{O} \leftrightarrow \text{MoO}_4^{3−} + 4\text{H}^+ 
\]

(10)

A Cary 5000i (Agilent) double-beam spectrophotometer was used for absorption measurements in dual-beam mode to correct for fluctuations due to electrical noise. Quartz cuvettes of path length 0.01, 0.1, 1.0, and 10 mm (Starna Cells) were used for measuring 0.3 M, 20 mM, 2 mM, and 0.1 mM Mo samples, respectively. Each sample was measured at room temperature (20 °C) against a blank reference solution with the corresponding HCl concentration to correct for the solvent absorbance peak exhibited just below 200 nm wavelength. It is important to note that the published tolerances of very-low-path-length open-cell cuvettes can be very high (10 μm ± 3 μm), posing a significant challenge to quantitative analysis. The path length of the "10-μm" cuvette was measured interferometrically, and the actual path length was 7.86 μm ± 0.5 μm.

The concentrations of chemical components that were determined by ICP−MS and acid−base titration were used to calculate ion activities. As thermodynamic data are based on activities, special care was taken to relate concentrations of chemicals to their thermodynamic activity. The complexities surrounding this relation are often avoided by performing experiments at constant, high ionic strength through the addition of nonparticipating ions to the solution. Such a simplification is not practical at the wide range of acid concentrations covered in these experiments. Therefore, activity coefficients were calculated for each solution using a modified semi-empirical Bromley method to allow stability constants to be calculated in reference to the infinite dilution standard state \( \left( I = 0 \text{ M} \right) \). The Argonne AMUSE code was used for this purpose.

Equilibrium constants and molar absorptivity spectra were calculated from the spectrophotometric data using the

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**Table 2. Species Abundance of Dinuclear Cations at 20 mM Mo + 1.0 M HCl with Increasing Chloride Concentration**

| [NaCl] (M) | MoO\(_2\)\(^{2+}\) + HMoO\(_2\)\(^{3+}\) (%) | HMoO\(_2\)Cl\(^2+\) (%) |
|------------|---------------------------------|----------------------------|
| 0          | 37                              | 12                         |
| 1.0        | 31                              | 19                         |
| 2.0        | 25                              | 23                         |
| 3.0        | 20                              | 27                         |
| 4.0        | 18                              | 28                         |

The results show that an increase in concentration of NaCl from 0 to 4 M leads to ~16% increase of HMoO\(_2\)Cl\(^2+\) species. This increase is accompanied by a ~19% decrease in the presence of nonchlorinated Mo dimers. These results indicate that an increase in total Cl\(^−\) concentration leads to a shift in the dimeric equilibria toward promotion of the chlorinated form while maintaining a near-constant total Mo dimer concentration in the investigated range of 0–4 M NaCl and 1 M HCl. This finding provides good support for the existence of HMoO\(_2\)Cl\(^2+\) by showing that the formation of an absorbing species not present in the molar absorptivity spectra for monomeric Mo shown in Figure 3 follows a clear dependence on [Cl\(^−\)] and thus is best explained by a chlorinated polynuclear complex. Analysis of the experimental spectra in the absence of a chlorinated dimer would not provide a satisfactory description of the increase in total absorbance at all wavelengths from 1 to 5 M Cl\(^−\). With the observation that the total dimer concentration in this region of HCl is maintained as the concentration of total chloride increases, the changes in spectral features presented in Figure 7 could only be supported by the increase in abundance of chlorinated dimers with higher molar absorptivity in the 220–260 nm region.

### Conclusions

Through chemometric analysis of UV spectrophotometric data, we have identified major Mo species in a wide range of Mo and HCl concentrations. In addition to previously reported monomeric Mo species present in HCl, the data suggest three dimeric Mo species present at concentrations above 0.1 mM Mo in HCl media. This study suggests the existence of a previously unreported chlorinated, cationic dimeric species stable up to ~6 M HCl at 300 mM Mo, with the general formula HMoO\(_2\)Cl\(^2+\).

At 0.1 mM Mo and 0.5–11 M HCl, monomeric Mo(VI) species predominate, with the contribution from dimeric species below 1%. As the Mo concentration increases up to 300 mM, absorbance spectra show the characteristic peak attributed to O−Mo−O bridging of cationic Mo dimers.
HypSpec program, which solves the nonlinear simultaneous mass balance equations using the Newton–Raphson method.\textsuperscript{21} A unit weighting scheme was applied to all spectrophotometric data. Data fitting was achieved by determining the parameters for which the objective function is minimized. Experimental error was estimated by the root mean square $\sigma$ of the residual $r$ values

\[
\sigma = \sqrt{\frac{\sum r_i^2}{n - m}} \tag{11}
\]

where $n$ is the number of data points and $m$ is the number of parameters. The expectation value of $\sigma$ in this case is zero, providing a universal index of goodness of fit. Speciation diagrams with known constants were modeled using HySS software, which belongs to the same HYPERQUAD program suite. Spectral data from previous authors used for comparison were extracted and interpolated (where necessary) by the cubic spline method using scikit image.\textsuperscript{22}

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The authors declare no competing financial interest.

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