Articles

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Equilibria and UV Spectra of Mono- and Polynuclear Molybdenum(VI) Species

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Molybdenum(VI) equilibria have been investigated in the pH_c range 2.3–6.1 by spectrophotometric titrations at 25 °C in 1.0 and 0.1 M (Na)Cl. The existence of a dimeric anion $HMo_2O_7^-$ with formation constant log $\beta_{2,3}$ = 14.6 ± 0.2 has been indicated by the results of computer treatment of the absorbance data. The following species, denoted by (p,q) according to the general formula $(MoO_4^{2-})_p(H^+)_q$, have been included in the reaction model: (1,0), (1,1), (1,2), (2,3), (7,8), (7,9), (7,10), and (8,12). Absorption spectra for all of these species have been calculated (206–300 nm) and are reported in the paper.

Introduction

As a result of various potentiometric and spectrophotometric studies of molybdenum(VI) equilibria in the pH_c region >2.5, a number of mono- and polynuclear species are now fairly well characterized with respect to formation constants.[1–5] These are the monomeric acids $HMoO_4^-$ and $Mo(OH)_6$,[6] the heptamolybdate ion, $Mo_7O_{24}^{6-}$, and its protonated forms $HMo_7O_{24}^{5-}$, $H_2Mo_7O_{24}^{4-}$, $H_3Mo_7O_{24}^{3-}$, and also the octamolybdate ion, $Mo_8O_{26}^{4-}$. A dimeric anion, $HMo_2O_7^-$, has been proposed recently[4] on the basis of potentiometric measurements and computer treatment of the data. Although the existence of such an anion seems reasonable in view of the occurrence of dimeric cations,[9–11] independent confirmation is needed by a method well suited for measurements at fairly low concentrations (ca. 10^{-4}–10^{-3} M). This consideration and general lack of information about the individual absorption spectra of the various polyanions have led us to undertake the present investigation. Apart from their intrinsic scientific value, these UV spectra are particularly useful for the interpretation of spectrophotometric data of molybdenum(VI) complex formation,[12,13] especially with ligands that do not absorb in the visible region. Indeed, without this information, quantitative treatment of the absorbance data can hardly be attempted. Sophisticated computer programs such as SQUAD,[14] SPECFIT,[15] and others[16] that are suitable for the treatment of spectrophotometric data, also of three-component systems, are now readily available.

Experimental Section

Reagents and Solutions. Analytical grade reagents (Merck p.a.) were used, and solutions were prepared with water obtained from a Millipore Milli-Q system. Sodium molybdate solution was prepared from the recrystallized salt and standardized by evaporating a suitable aliquot to dryness and heating to constant weight at 160 °C. Sodium chloride was purified as follows. A saturated solution was allowed to stand for 1 week and then filtered. Relatively large and pure crystals were obtained by allowing this filtrate to evaporate at ca. 25 °C for several weeks. The crystals were filtered off and washed twice with ice-cold water. Stock solutions prepared from the recrystallized sodium chloride were standardized by evaporating known volumes to dryness and heating at 160 °C to constant weight. Hydrochloric acid was standardized indirectly against potassium hydrogen phthalate by titration with sodium hydroxide.

Spectrophotometric and Potentiometric Measurements. The spectrophotometric measurements were made with a Varian Cary 210 spectrophotometer. The solution to be examined was circulated by means of a peristaltic pump from a reaction vessel in a thermostated water bath to a variable path length flow-through cuvette, and the spectra were recorded vs. air. The correct path length at each setting was obtained by calibration as described previously.[17] Adjustment of the solution pH was achieved by following a titration procedure. Experiments were performed at two constant ionic strengths, namely 1.0 and 0.1 M (NaCl). In the former case, solutions of the following four initial molybdate concentrations, each 1.0 M in NaCl, were titrated (cuvette path lengths are given in parentheses): 0.2337 (0.6026 cm), 0.4720 (0.3026 cm), 1.493 (0.1026 cm), and 4.398 mM (0.0326 cm). In each case, the reaction vessel was charged with 90.00 mL of the molybdate solution and the titration carried out with 0.1000 M HCl (0.9 M in NaCl). In the series of four titrations, the pH_c was varied between a maximum of 6.06 and a minimum of 2.32. The total molybdenum concentration decreased by ≤8% in the course of the titrations. Altogether, 41 spectra were recorded at 2-nm intervals between 206 and 300 nm, giving 1968 data points. In the second experiment 90.00 mL of a 7.5×10^{-5} M sodium molybdate solution (0.1 M in NaCl) was titrated with 0.1000 M hydrochloric acid, also 7.5×10^{-5} M in sodium molybdate. Thus the total molybdenum(VI) concentration was kept constant while the pH_c was varied between 5.75 and 2.65. In this experiment a 1.00-cm fixed-path flow-through cuvette was used. A total of 17 spectra were recorded at 2-nm intervals in the range 202–300 nm, giving 850 data points. Blank absorbance corrections were made by subtracting the absorbances of the pure sodium chloride solution (1 or 0.1 M) recorded in the same fashion as absorbances of the test solutions.

To obtain free hydrogen ion concentrations, the potential of each test solution was measured to ±0.1 mV with a Radiometer PHM84 Research pH meter using a Ross (Orion) electrode. The following equation was used to calculate the free hydrogen ion concentration, h, from the measured potential E (in mV):

$$E = E° - 59.15 \log h \qquad (1)$$

For brevity, $-\log h$ is denoted by pH_c. A value of $E°$ was determined for the different ionic media by titrating 0.1 and 1.0 M NaCl solutions with 0.1 M HCl and 0.1 M HCl + 0.9 M NaCl, respectively.

Results and Discussion

Calculations. The simultaneous protonation and condensation equilibria established upon acidification of molybdate can be represented by the general equation

(1) Aveston, J.; Anacker, E. W.; Johnson, J. S. *Inorg. Chem.* **1964**, *3*, 735.
(2) Sasaki, Y.; Sillén, L. G. *Ark. Kemi* **1968**, *29*, 253.
(3) Cruywagen, J. J.; Rohwer, E. F. C. H. *Inorg. Chem.* **1975**, *14*, 3136.
(4) Cruywagen, J. J. *Inorg. Chem.* **1980**, *19*, 552.
(5) Tytko, K. H.; Baethe, G.; Cruywagen, J. J. *Inorg. Chem.* **1985**, *24*, 3132.
(6) The formula $Mo(OH)_6$ is used to indicate octahedral coordination. There is reason to believe that molybdic acid is better formulated as $[MoO_2(H_2O)_2(OH)_2]$[7] or even $[MoO_3(H_2O)_3]$.[8] Because of uncertainties about the location of the protons in the protonated polyanions, the conventional formulas are used, e.g. $HMo_7O_{24}^{5-}$ instead of $[Mo_7O_{23}(OH)]^{5-}$; the latter formula implies protonation of a terminal oxygen atom.
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(17) Choat, T. C.; Cruywagen, J. J.; Heyns, J. B. B. *Anal. Chem.* **1986**, *58*, 2571.

$$pMoO_4^{2-} + qH^+ = (MoO_4^{2-})_p(H^+)_q \qquad (2)$$
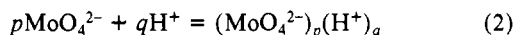
For convenience a species with overall formation constants $\beta_{p,q}$ is often herein represented by the stoichiometric coefficients that define its composition, e.g. (7,8) for the $Mo_7O_{24}^{6-}$ ion.

The computer program SPECFIT[15] was used to treat the absorbance data. The ionic medium 1 M NaCl was chosen for the measurements to facilitate correlation of the absorbance data with results of previous potentiometric investigations pertaining to this medium.[4,5] In point of fact, the large number of species to be taken into account together with the great similarity between the spectra of the various polynuclear species practically precludes complete characterization of the system from spectrophotometric data alone. Some constants from potentiometric experiments have hence been utilized in the present calculations.

Calculations were started with a reaction model comprising molybdate and the following seven species: (1,1), (1,2), (2,3), (7,8), (7,9), (7,10), and (8,12). This model gave the best fit to potentiometric data in a previous study for which the ionic medium was also 1 M NaCl.[4] As the spectrum of molybdate can be measured directly at a suitable pH_c and concentration (i.e. under conditions where protonation and condensation can be neglected) and that of monomeric molybdic acid is reliably known from previous work,[18] the spectra of these two species could be treated as known quantities and were therefore fixed in the first computations. Except for that of the (2,3) ion, whose existence needed verification, the formation constants of the other species included in the model are known with sufficient certainty to be treated as fixed parameters. However, as a check on the reliability of the data, some of these constants were calculated in turn together with the six unknown spectra. The values so obtained for the constants agreed well with those determined previously by potentiometry. It was also found that inclusion of the dimeric anion (2,3) resulted in a better fit between experimental and calculated absorbances. Compare for example the result[19]

$\log \beta_{7,9} = 57.6 \pm 0.1 \qquad \log \beta_{2,3} = 15.0 \pm 0.4 \qquad \sigma_A = 0.082$
$\log \beta_{7,9} = 57.5 \pm 0.2 \qquad \qquad \ldots \qquad \qquad \sigma_A = 0.091$

The values previously obtained by potentiometry[4] for these constants are $\log \beta_{7,9} = 57.45$ and $\log \beta_{2,3} = 14.8$. The satisfactory agreement between the $\log \beta_{2,3}$ values can be regarded as strong evidence for the existence of the (2,3) species. The spectrum calculated for the (1,1) species in most of the runs was however not satisfactory; its reproducibility was poor and the uncertainties in the calculated molar absorption coefficients were much greater than those of the polyanions (e.g. 13% and 3%, respectively, at 240 nm). The most important reason for this unsatisfactory result was that the (1,1) ion occurred in relatively low concentrations, reaching a maximum of 10–20% of the total molybdenum concentration in only five solutions (i.e. five experimental spectra). This uncertainty in the spectrum of the (1,1) species appeared to have some effect on the reliability of the spectrum calculated for the (2,3) species, because of appreciable overlap of the two equilibria.

It was therefore decided that another experiment be performed under conditions where only mononuclear species would be present in order to obtain the most accurate spectrum for the (1,1) species for use in the calculations. For this spectrophotometric titration an ionic strength of 0.1 M was chosen for two specific reasons. First, to ensure that polyanions can be neglected, an extremely low molybdenum concentration must be used in which case it is advantageous also to have a low blank absorption, especially at wavelengths <220 nm, where absorption of sodium chloride is significant. Second, by reducing the ionic strength, the relative amounts of polyanions at a given molybdenum concentration are
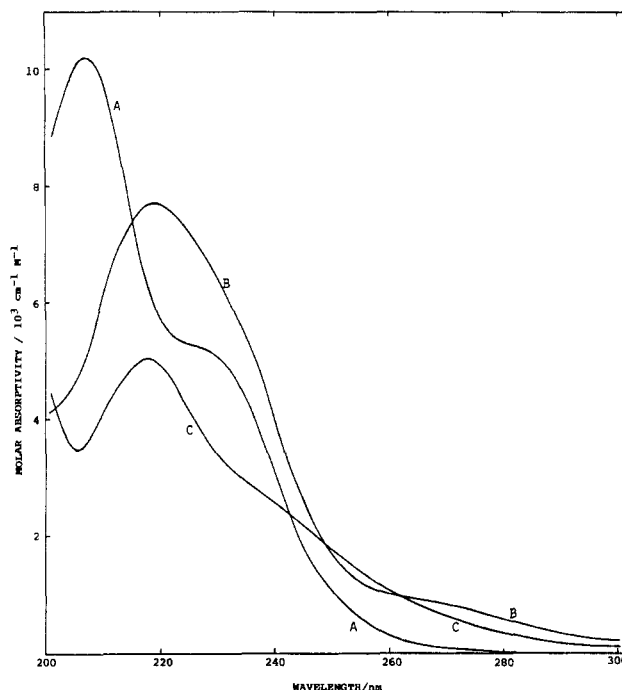

Figure 1. UV spectra of the monomers MoO_4^{2-} (A), $HMoO_4^-$ (C), and $Mo(OH)_6$ (B).

lowered due to the expected smaller values of their equilibrium constants.[5] Assuming that the (2,3) species has a formation constant of about 1 log unit lower in 0.1 M NaCl, and using for the other species constants pertaining to 1 M NaCl, calculations showed that the relative amounts of polyanions were negligible compared to that of the mononuclear species at a molybdenum concentration of 7.5×10^{-5} M.

In the treatment of the data of this titration (17 experimental spectra), the spectra of the three monomers and formation constants of the (1,1) and (1,2) species were calculated. An excellent fit between experimental and calculated absorbances was obtained, resulting in very low standard deviations for the equilibrium constants ($\log \beta_{1,1} = 3.66 \pm 0.01$ and $\log \beta_{1,2} = 7.47 \pm 0.01$) and small uncertainties in the calculated molar absorption coefficients ($\sigma_A = 1.06 \times 10^{-3}$); the spectra are shown in Figure 1. This very good fit implies that the calculations were based on the correct reaction model and that neglect of the (2,3) species was justified. A subsequent run with inclusion of the (2,3) species provided a "value" $\log \beta_{2,3} = 13.4$, implying a maximum share for this species of <0.8% of the total molybdenum concentration, and accordingly absurd values for the molar absorption coefficients were produced.

The spectra of both the (1,1) and (1,2) species thus obtained were used together with that of MoO_4^{2-} as known quantities in all further calculations. In the first run, using all data pertaining to 1 M NaCl, the formation constants were fixed at their potentiometric values to calculate spectra for the polyanions. This resulted in a good fit of theoretical to experimental absorbances and provided satisfactory (preliminary) spectra. Several more runs were done to acquire additional and as far as possible independent proof for the existence of the (2,3) species and also to obtain the most accurate spectrum for each of the polyanions. The results of a number of these runs, which among other things convey the characteristics and complexity of the system, are briefly discussed in what follows:

(1) All formation constants and spectra (except those of the monomers) were treated as unknowns. Although the estimated standard deviations were totally unacceptable, surprisingly, the values for most of the constants agreed satisfactorily with those derived by potentiometry (Table I, run A). The spectra were likewise unacceptable; absorption coefficients at some wavelengths were disproportionately large or small or even negative. Evidently the number of unknowns had to be reduced by fixing some of the formation constants at values determined by potentiometry (cf.

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(19) The data for the various concentrations were normalized to a path length of 1.00 cm, resulting in much higher absorbances than the measured values. Accordingly, σ_A values for calculations involving high Mo(VI) concentrations (short path lengths) are much greater than σ_A pertaining to low concentrations only.

Table I. Values of Formation Constants Calculated in Computer Runs (Cf. Text for Explanation)

run	log $\beta_{1,1}$	log $\beta_{1,2}$	log $\beta_{2,3}$	log $\beta_{7,8}$	log $\beta_{7,9}$	log $\beta_{7,10}$	log $\beta_{8,12}$	$10^2\sigma_A$
pot.[a]	3.39 ± 0.05	7.16 ± 0.05	14.81 ± 0.10	52.80 ± 0.01	57.45 ± 0.01	60.77 ± 0.06	71.53 ± 0.10	...
A	3.4 ± 5.1	7.1 ± 5.1	14.3 ± 4.3	53.0 ± 4.4	57.6 ± 4.6	58.6 ± 2.9	71.5 ± 4.3	9.0
B	b	b	b	52.8 ± 0.3	57.7 ± 0.1	58.8 ± 3.1	71.7 ± 0.3	9.2
C	3.42 ± 0.03	7.20 ± 0.02	14.36 ± 0.15	b	57.61 ± 0.09	b	b	9.1

[a] Potentiometrically derived values.[4] Error limits are 3σ. [b] Fixed at the potentiometric value.
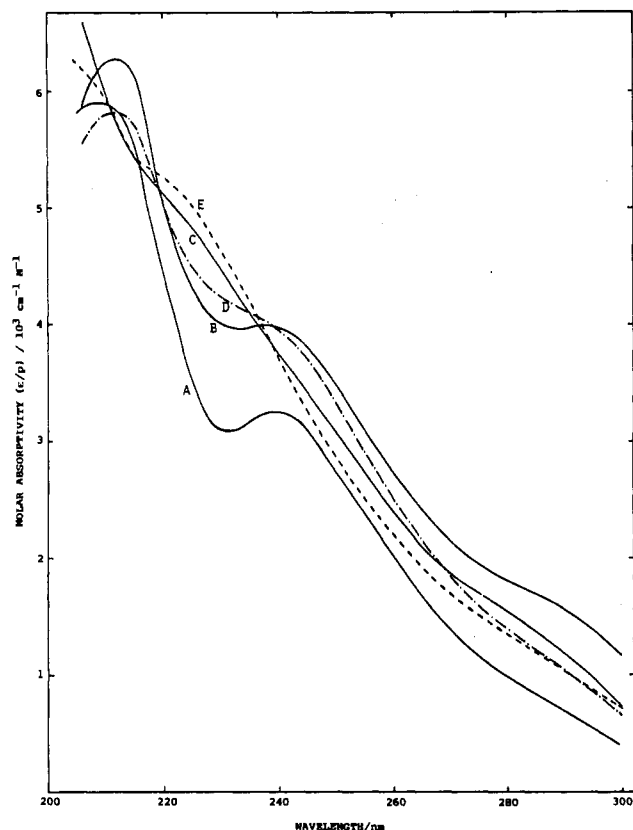
Figure 2. UV spectra (ϵ/p) of the polyanions $HMo_2O_7^-$ (A), $Mo_7O_{24}^{6-}$ (B), $HMo_7O_{24}^{5-}$ (C), $H_2Mo_7O_{24}^{4-}$ (D), and $Mo_8O_{26}^{4-}$ (E).

Figure 3. Distribution of species as a function of pH_c at molybdenum(VI) concentration 2.337×10^{-4} M. For clarity the (7,8) and (8,12) distributions are omitted; their percentages are below 5%.

Table I, runs B and C). A similar calculation with exclusion of the (2,3) species showed cyclic behavior and hence failed to converge while the sum of squares was significantly greater (15.6 vs. 14.0) than for the run that included the dimer.

(2) Two more runs were done to further improve the quality of the spectra of all the polynuclear species. Spectra for the latter species were calculated by using only the titration data at the highest molybdenum concentration, where the contributions of the monomeric species and the dimer are practically negligible while the heptamers and octamer occur in their highest relative concentrations. Equilibrium constants of all species were fixed at known potentiometric values, and for the (2,3) species its preliminary spectrum was used. These spectral curves are shown in Figure 2.

In the next run the objective was to obtain the "best" possible spectrum for only the (2,3) species. From the titrations at the two lowest molybdenum concentrations twelve experimental spectra of solutions in which the dimer attains its highest concentration were selected to calculate its spectrum and formation constant. The best spectra of the other polyanions obtained in the previous run were introduced as known quantities, and the values of all equilibrium constants other than $\beta_{2,3}$ were fixed. The spectrum thus calculated for the dimer is shown in Figure 2; the value of the formation constant was log $\beta_{2,3}$ = 14.6 ± 0.1.

(3) The absorbance data of the lowest molybdenum concentration $(2.337 \times 10^{-4}$ M) for which the hepta- and octanuclear species are relatively unimportant (Figure 3) were used for a final check on the validity of the reaction model. The spectra and formation constants of the latter species were fixed, the (2,3) species was not taken into account, and the equilibrium constants
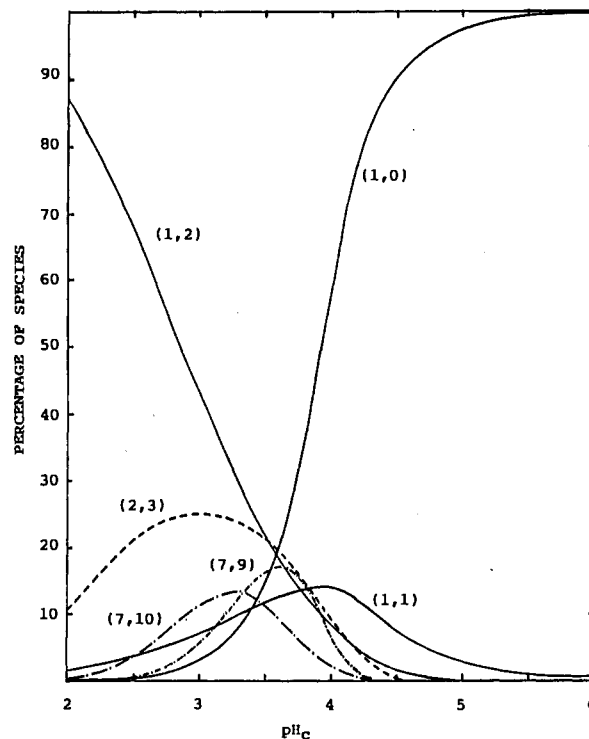
of the monomers were calculated. Then the (2,3) species was added to the model and the calculations were repeated. This led to a significant improvement of the fit, σ_A being reduced from 8.31×10^{-3} to 6.75×10^{-3}.

Spectra of Various Species. The spectra of the mononuclear species are shown in Figure 1. It is seen that protonation of molybdate, first to bimolybdate and then to molybdic acid, results in a considerable change in absorption. The spectrum of molybdate like that of other tetrahedral d° transition-metal oxyanions (e.g. VO_4^{3-}, CrO_4^{2-}, and WO_4^{2-}) arises as a consequence of light absorption due to transfer of an electron from an orbital primarily on the oxygen to one primarily on the metal.[20] As the wavelengths at which these charge-transfer bands occur depend on the oxidizing power of the metal, the two absorption peaks of CrO_4^{2-} for example appear at longer wavelengths (lower energy) than those of MoO_4^{2-}.[20] The intensities of the bands for the two ions are inverted, and the energy difference between the molybdate bands is smaller. Thus the long-wavelength band of molybdate is observed as a shoulder in the spectrum and has about the same intensity as the corresponding CrO_4^{2-} band, but the short-wavelength band of molybdate is about 2.5 times more intense than that of chromate.

When in these anions an oxo ligand is replaced by the less basic hydroxo ligand, more energy would be required for charge transfer to the metal and the charge transfer bands would therefore be expected to shift to shorter wavelengths. Accordingly, when CrO_4^{2-} is protonated to $HCrO_4^-$, both bands are displaced to shorter wavelengths; a new band of much lower intensity on the long-wavelength side of the other two bands also appears in the

(20) Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: Amsterdam, 1984; and references cited.

$HCrO_4^-$ spectrum.[21] Very similar changes are observed when MoO_4^{2-} is protonated. Apparently the shoulder of the molybdate spectrum at 228 nm (43 860 cm^{-1}) appears as a peak at 218 nm (45 870 cm^{-1}) in the bimolybdate spectrum while the maximum of the molybdate spectrum at 207 nm (48 300 cm^{-1}) is shifted for bimolybdate to wavelengths <200 nm (50 000 cm^{-1}) where it cannot be measured in aqueous solution. A new and weaker band also appears in the bimolybdate spectrum as a shoulder on the long-wavelength side of the other two bands. Therefore, except for a greater decrease in the intensities of the chromate bands, the changes brought about by protonation are very similar for molybdate and chromate, an observation which supports the thermodynamic evidence that bimolybdate is tetrahedral rather than octahedral.[3]

Protonation of bimolybdate to monomeric molybdic acid involves an increase in the coordination number from 4 to 6 for molybdenum. The spectrum of $Mo(OH)_6$ shows only one prominent band at 219 nm, which is much broader and also is of higher intensity than the band of $HMoO_4^-$ that occurs at the same wavelength. When $Mo(OH)_6$ is converted into the monomeric cation $Mo(OH)_5H_2O^+$ on further protonation, the intensity of this band is decreased and an expected shift to shorter wavelengths occurs.[18] From the foregoing it is seen that the different spectra reveal very little information about the structure of the various protonated species. Application of molecular orbital theory, however, might provide useful insights if structural and bonding characteristics of the various protonated species can be successfully related to the observed changes in absorption bands.[20,21]

The spectrum of the dimeric anion (represented in terms of $\epsilon/2$, in Figure 2), showing a weak band at $\sim$242 nm and stronger absorbance at shorter wavelengths, can be compared with the spectra of molybdenum(VI) dimeric cations that have absorption bands at 243–248 nm.[9-10] The spectrum of the dimeric oxalato complex $Mo_2O_5(C_2O_4)_2(H_2O)_2^{2-}$ also exhibits a shoulder at these wavelengths.[13]

The spectra of the heptamers and octamer (ϵ/p) do not show great differences. Insofar as the structures of these ions are considered as being composed of MoO_6 octahedra, this is to be expected. In the wavelength range 290–300 nm where absorption of the monomeric species is insignificant, these spectra have weak absorption bands. It is seen that both the heptamolybdate ion $Mo_7O_{24}^{6-}$ and its doubly protonated form $H_2Mo_7O_{24}^{4-}$ have a maximum at $\sim$212 nm and a shoulder at $\sim$238 nm, respectively, the shoulder of $Mo_7O_{24}^{6-}$ being more prominent. The spectrum of $HMo_7O_{24}^{5-}$ does not exhibit any characteristic bands, while that of $Mo_8O_{24}^{4-}$ has a shoulder at $\sim$222 nm and presumably a maximum at a wavelength somewhat below 200 nm.

The spectra of these ions are quite different from that of the $Mo_6O_{19}^{2-}$ ion, which has characteristic absorption peaks at three wavelengths, 222, 257, and 325 nm.[22,23] The structure of this ion, which does not occur in significant amounts in aqueous so-

lution but is very stable in some nonaqueous solvents such as tributyl phosphate or methyl cyanide, is unique in that each of its six MoO_6 octahedra has only one terminal (unshared) oxygen atom.[24] The structure (β form) of $Mo_8O_{26}^{4-}$ does have one octahedron with a single terminal oxygen,[25,26] but apart from the shoulder at $\sim$222 nm, its spectrum does not resemble that of $Mo_6O_{19}^{2-}$.

Conclusion

Quantitative treatment of the spectrophotometric data has provided strong evidence for the existence of a (2,3) species, i.e. a dimeric anion $HMo_2O_7^-$. Discrete $Mo_2O_7^{2-}$ ions, consisting of two MoO_4 tetrahedra sharing a common vertex, which are stable in the nonaqueous solvent CH_3CN,[27] do not occur in aqueous solution, at least not in measurable quantities. The singly charged dimer, $HMo_2O_7^-$, may well owe its stability in aqueous solution to an expansion of the coordination number of at least one of the molybdenum atoms, thereby enabling it to compete more successfully with other polyanions of the same degree of protonation. In the case of monomeric molybdate the change from tetrahedral to octahedral coordination by the uptake of two water molecules occurs only in the second protonation step, that is after the negative charge on molybdate has been reduced to less than 1.[3] The structure of the singly charged dimer $HMo_2O_7^-$ could therefore be visualized as consisting of two octahedral units (or perhaps one octahedron and one tetrahedron) linked by sharing an oxygen atom, as is the case for the dimeric complex anion[28] Mo_2O_5-$(C_2O_4)_2(H_2O)_2^{2-}$.

The individual UV absorption spectra of seven species have been calculated that clearly show the difference between the characteristic bands of mono- and polynuclear species. Although the individual spectral curves of the polyanions will be slightly affected by small uncertainties in the values of the formation constants, and perhaps also by the presence of very small amounts of still unidentified minor species, these spectra give an excellent description of the experimental data and can therefore be used with confidence in spectrophotometric studies, e.g. when needed to provide for the absorbance of molybdenum(VI) species in equilibrium studies of complex formation.

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