

Molybdenum(vi) Complex Formation. Part 6.¹ Reactions with Aspartate in 1.0 mol dm⁻³ Sodium Chloride Medium at 25 °C

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Complex formation between molybdate and aspartate $^{-}\text{O}_2\text{CCH}_2\text{CH}(\text{NH}_2)\text{CO}_2^{-}$ (L^{2-}) has been investigated in the pH range 1.2–7.5 by potentiometric, spectrophotometric and enthalpimetric titrations at 25 °C in 1.0 mol dm⁻³ NaCl. The 'best' reaction model, based on computer treatment of the data and supported by analysis of spectrophotometric measurements, comprises nine complexes representing various stoichiometries. The formation constants of the complexes, denoted by β_{pqr} , where the subscripts p , q and r refer to the stoichiometric coefficients in the general formula $[(\text{MoO}_4)_p(\text{HL})_q\text{H}_r]^{(2p+q-r)-}$, have the values $\log \beta_{111} = 6.54$, $\log \beta_{112} = 9.84$, $\log \beta_{121} = 6.57$, $\log \beta_{122} = 11.47$, $\log \beta_{214} = 21.20$, $\log \beta_{215} = 23.50$, $\log \beta_{248} = 37.74$, $\log \beta_{449} = 50.86$ and $\log \beta_{4410} = 53.48$. Enthalpy and entropy changes for the major complexes were calculated from the calorimetric data using these formation constants: $\Delta H^\circ_{111} = -26.8$, $\Delta H^\circ_{122} = -38$, $\Delta H^\circ_{214} = -97$ and $\Delta H^\circ_{215} = -83$ kJ mol⁻¹. Thermodynamic parameters for the protonation of aspartate in 1.0 mol dm⁻³ NaCl have also been determined: $\log \beta_{011} = 3.64$ and $\log \beta_{012} = 5.65$; $\Delta H^\circ_{011} = -5.8$ and $\Delta H^\circ_{012} = -10.2$ kJ mol⁻¹.

The formation in aqueous solution of a complex having a molybdate to aspartate ratio of 1:1 has been suggested by Brown and McPherson² and subsequently confirmed by other workers.^{3–7} A formation constant for the complex, formulated⁴ as $[\text{MoO}_3\text{L}]^{2-}$, where $\text{L}^{2-} = ^{-}\text{O}_2\text{CCH}_2\text{CH}(\text{NH}_2)\text{CO}_2^{-}$, has been determined by potentiometry³ and spectrophotometry⁴ at pH ≈ 6 where interference of molybdenum(vi) polyanion formation is negligible; the values reported for the constants differed by about one log unit. Stepwise stability constants for the formation of 1:1, 1:2 and 1:3 molybdate:aspartate complexes have also been reported,⁷ but the results have been questioned,^{3,4} mainly because molybdenum(vi) side-equilibria had been neglected (*cf.* Results and Discussion section). A white complex with composition $\text{K}_2[\text{MoO}_3\text{L}]\cdot\text{H}_2\text{O}$ has been isolated from a solution containing sodium molybdate and aspartic acid at pH 6.⁵ Recently, while the present study was in progress,[†] the results of a spectrophotometric and potentiometric investigation extending to pH 2 have been reported.⁸ In addition to the mononuclear complex mentioned above, three dinuclear complexes were postulated, $[\text{Mo}_2\text{O}_5\text{L}_2]^{2-}$, $[\text{Mo}_2\text{O}_4(\text{OH})\text{L}_2]^{-}$ and $[\text{Mo}_2\text{O}_4\text{L}_2]$ for which stability constants were determined. Apart from equilibrium constants no thermodynamic quantities for any of the species have been determined.

In this paper we report the results of a comprehensive potentiometric, spectrophotometric, and enthalpimetric investigation of molybdenum(vi)–aspartate complex formation in the range pH 7.5–1.2. Equilibrium analysis of the data using the computer programs SUPERQUAD⁹ and SPECFIT¹⁰ verified the existence of the mononuclear complex $[\text{MoO}_3\text{L}]^{2-}$ but led to the identification of several complexes not previously reported for this system. Enthalpy and entropy changes for the major complexes have been calculated from the enthalpimetric data.

Experimental

Reagents and Solutions.—All reagents were of analytical

grade (Merck and BDH) and solutions were prepared with water obtained from a Millipore Milli-Q system. Sodium molybdate stock solution was prepared from the recrystallized salt $\text{Na}_2\text{MoO}_4\cdot 2\text{H}_2\text{O}$ and standardized gravimetrically as described previously.¹¹ Sodium chloride was purified as described previously.¹¹ L-Aspartic acid (BDH) was used as received. Hydrochloric acid was standardized indirectly against potassium hydrogenphthalate by titration with sodium hydroxide.

Potentiometric Titrations.—Mixtures of sodium molybdate, aspartic acid and sodium hydroxide (70–90 cm³) were titrated with hydrochloric acid at 25 °C using a Metrohm 636 Titroprocessor. All solutions were made 1.0 mol dm⁻³ with respect to chloride ions by addition of the appropriate amount of recrystallized sodium chloride. To exclude carbon dioxide from the system a stream of purified nitrogen was passed through 1.0 mol dm⁻³ NaCl and then bubbled slowly through the titration solution. The initial concentrations (mol dm⁻³) of molybdate and aspartate were as follows: 0.005, 0.1; 0.005, 0.05; 0.01, 0.05; 0.02, 0.10; 0.05, 0.25 and 0.005, 0.01 thus giving a 20-, 10-, 5- and 2-fold excess of aspartate over molybdate; the pH_c range covered was 7.5–1.2. In another series of experiments aspartate solutions (0.10 mol dm⁻³) acidified to pH_c ≈ 1.8 , 2.2, 2.6 and 3.5 respectively were titrated with molybdate (0.10 mol dm⁻³) up to a ratio of 1:5 for molybdate:aspartate. In one titration the ratio of molybdate:aspartate was kept constant but the concentrations increased from 0.005:0.025 to 0.025:0.125 mol dm⁻³ while the pH_c varied from 6.9 to 5.2. For the determination of the protonation constants of aspartate, a solution of aspartic acid (or the neutralized acid) was titrated with sodium hydroxide (or hydrochloric acid) covering the pH_c range 1.0–10.8. All titrations were carried out in duplicate.

The free hydrogen ion concentration, h , was determined by measuring the potential, E° , to ± 0.2 mV using a Ross combination electrode (Orion) with a 3.0 mol dm⁻³ KCl bridge solution. Equation (1) was used to calculate h from the measured potential at each titration point.

$$E = E^\circ + 59.16 \log h + E_j \quad (1)$$

[†] Part of this work has been presented at the XVII ICCS, Broadbeach, Australia, 1989.

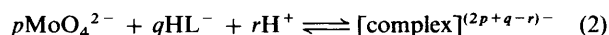
Values for E° and E_j were determined from titrations of 1.0 mol dm⁻³ NaCl with HCl as described by Rossotti.¹² For brevity $-\log h$ is denoted by pH_c .

Calorimetric Titrations.—An isothermal calorimeter, Tronac model 550, described elsewhere¹³ was used for the enthalpy measurements. Solutions containing molybdate and aspartate (20.0 cm³) were titrated with hydrochloric acid from a precision microburette (2.5 cm³) and the data collected as described previously.¹¹ The initial concentrations of molybdate and aspartate were 0.01 and 0.10 mol dm⁻³ respectively; the pH_c range covered was 6.0–2.6. A separate titration of sodium aspartate (0.10 mol dm⁻³) with hydrochloric acid (1.0 mol dm⁻³) was done to determine the enthalpy involved in the protonation of aspartate. All solutions were made 1.0 mol dm⁻³ with respect to chloride by addition of the appropriate amount of recrystallized sodium chloride. Titrations were carried out in triplicate. The data were corrected for the endothermic heat of dilution of hydrochloric acid titrated into sodium chloride by using results of previous blank titrations.^{11,14}

Spectrophotometric Titrations.—A Varian Cary 210 spectrophotometer in conjunction with an Apple IIe computer was used for the absorption measurements and data collection. Two titrations were carried out. For the first titration the concentrations of molybdate and aspartate were 0.005 and 0.10 mol dm⁻³ respectively and for the second titration 0.01 and 0.10 mol dm⁻³. The titrant solution contained in addition to hydrochloric acid also aspartate and molybdate at the same concentration as the test solution. The ionic medium was 1.0 mol dm⁻³ NaCl. The absorbances were measured against air in the wavelength range 222–300 nm using a flow through cuvette¹⁵ with adjustable path length. The path length (calibrated) was set at 0.024 82 cm for both experiments. Blank absorbances were obtained from a similar titration of a solution without molybdate. In the range 222–300 nm absorption of aspartic acid and its ionization products at the chosen path length is small and shows only a small dependence on pH_c below 230 nm. The absorbance of aspartate starts to increase rapidly with decrease in wavelength below 220 nm. The temperature in the reaction vessel and cell compartment was kept constant at 25 °C. The hydrogen ion concentration was measured as described for the potentiometric titrations. Twenty spectra were measured in each experiment at pH_c intervals of ≈ 0.25 in the range 7–2.3.

Results and Discussion

Potentiometric Investigation.—The various protonation, condensation and complexation reactions that can take place when a solution containing molybdate and aspartate is acidified are represented by the general equation (2). The equilibria are



formulated in terms of HL^- rather than L^{2-} ; the latter ion is already completely converted to HL^- at the pH_c (≈ 6.5) where complex formation begins.

For brevity species with overall formation constants β_{pqr} will often be described by the stoichiometric coefficients defining their composition, for example [0,1,1] for neutral aspartic acid.

Although the overall stoichiometry and charge of these complexes are adequately described by the p , q and r coefficients, as determined by potentiometry, their correct formulation is not straightforward and has to be based on chemical knowledge and other experimental methods.

The results of some representative titrations of aspartate and of mixtures of molybdate and aspartate with hydrochloric acid are shown in Fig. 1 as plots of F against pH_c . The function $F = (H - h)/(2B + C)$ represents the fraction of the total negative charge neutralized due to protonation where H , B and

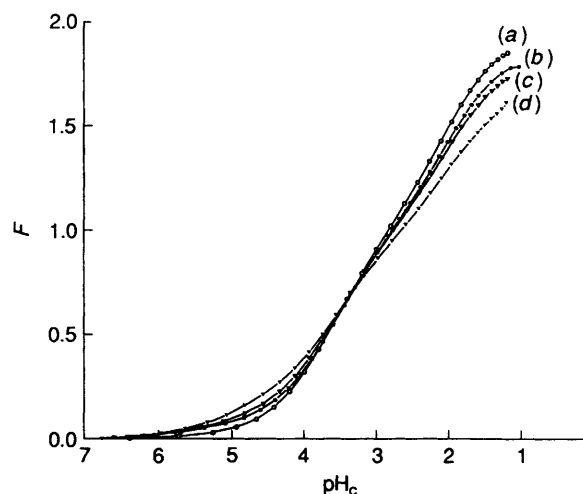


Fig. 1 Plots of function F versus pH_c for some representative potentiometric titrations. Initial concentrations (molybdate:aspartate): (a) 0.05:0.10, (b) 0.005:0.05, (c) 0.005:0.1 and (d) 0.00:0.05 mol dm⁻³

C are the analytical concentrations of acid, molybdate and aspartate respectively.

An F value of 1.0 therefore indicates an average charge of zero for the species in solution. This is the case at $\text{pH}_c \approx 3$ where H_2L is the major component. A decrease in pH_c causes further protonation of aspartic acid until at $\text{pH}_c \approx 1$ more than 80% is in the form of H_3L^+ . The effect of complexation on the uptake of protons is indicated by the change in the F curves (Fig. 1) with increasing molybdenum(vi) concentration. At low pH_c protonation of complex species is more difficult than that of aspartate whereas the opposite is true at high pH_c ; the crossover point is at $\text{pH}_c \approx 3.3$. Compared to some other carboxylate ligands previously investigated *e.g.* oxalate¹¹ or tartrate,¹⁴ complexation of aspartate with molybdenum(vi) is rather weak and titrations were done with aspartate in excess. It turned out that at least a ten-fold excess of aspartate was required to reduce the concentrations of uncomplexed protonated and condensed molybdate species to less than 7% in the pH_c range investigated. In the treatment of the data it was therefore important to take into account all side-equilibria of molybdate and aspartate. The molybdate species $[\text{HMoO}_4]^-$, $[\text{MoO}_3(\text{OH})_2]_3$, $[\text{MoO}_2(\text{OH})(\text{OH}_2)_3]^+$, $[\text{HMo}_2\text{O}_7]^-$, $[\text{Mo}_7\text{O}_{24}]^{6-}$, $[\text{HMo}_7\text{O}_{24}]^{5-}$, $[\text{H}_2\text{Mo}_7\text{O}_{24}]^{4-}$, $[\text{H}_3\text{Mo}_7\text{O}_{24}]^{3-}$, $[\text{Mo}_8\text{O}_{26}]^{4-}$ and $[\text{HMo}_2\text{O}_6]^+$ were taken into account using previously determined equilibrium constants pertaining to 1.0 mol dm⁻³ NaCl or NaClO₄ medium at 25 °C.^{16–18} The protonation constants of aspartate in 1.0 mol dm⁻³ NaCl were determined in separate titrations. The values obtained, $\log \beta_{011} = 3.640 \pm 0.004$ and $\log \beta_{012} = 5.654 \pm 0.006$, are in good agreement with those reported for 1.0 mol dm⁻³ NaClO₄, namely $\log \beta_{011} = 3.69 \pm 0.02$ and $\log \beta_{012} = 5.80 \pm 0.03$.¹⁹

The potentiometric data were treated with the program SUPERQUAD⁹ to search for the reaction model that would give the best description of the data. The program automatically rejects species for which the relative standard deviation of the formation constant is greater than 33% (or $3\sigma \geq 0.43$ log units). All possible species with $p = 1$ –4 and having reasonable q and r values have been considered in various reaction models. The $[1,1,1]^{2-}$ complex could be easily identified as the first major complex that forms upon acidification of a mixture of molybdate and aspartate. Its inclusion in a particular model invariably caused a considerable improvement in the fit while the standard deviation of its stability constant was significantly smaller than that of any other species considered. Selection of the other complexes was not straightforward. As mentioned above, an excess of ligand is a prerequisite but it turned out that some of the most likely complexes in the model have a stoichiometry for which the optimum conditions would be

Table 1 Values for the formation constants and thermodynamic quantities (kJ mol^{-1}) in 1 mol dm^{-3} NaCl at 298.15 K for the complexes in the 'best' reaction model

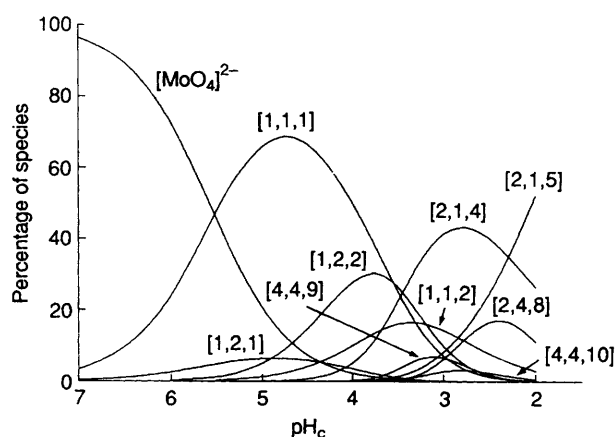
Complex	$(\log \beta \pm 3\sigma)$	ΔG°	ΔH°	$T\Delta S^\circ$
$[1,1,1]^{2-}$	6.54 ± 0.01	-37.3	-26.8 ± 0.4	10.5 ± 0.4
$[1,1,2]^-$	9.84 ± 0.12	-56.2	$(-26.8)^*$	(29)
$[1,2,1]^{3-}$	6.57 ± 0.10	-37.5	—	—
$[1,2,2]^{2-}$	11.47 ± 0.04	-65.5	-38 ± 2	28 ± 2
$[2,1,4]^-$	21.20 ± 0.05	-121.0	-97 ± 8	24 ± 8
$[2,1,5]^-$	23.50 ± 0.05	-134.1	-83 ± 10	51 ± 10
$[4,4,9]^{3-}$	50.86 ± 0.11	-290.3	$(-126 \pm 40)^*$	(164 ± 40)
$[4,4,10]^{2-}$	53.48 ± 0.34	-299.6	$(-126 \pm 40)^*$	(174 ± 40)
$[2,4,8]^-$	37.74 ± 0.10	-215.4	-62 ± 30	153 ± 30
$[0,1,1]^-$	3.64 ± 0.01	-20.8	-5.8 ± 0.2	15.0 ± 0.2
$[0,1,2]^+$	5.65 ± 0.01	-32.3	-10.2 ± 0.6	22.1 ± 0.6

* Values in parentheses are approximate; see text.

Table 2 Results of some model tests with SUPERQUAD; improvement in fit indicated by s value, given in the last line

$[1,1,1]^{2-}$	$[1,1,1]^{2-}$	$[1,1,1]^{2-}$	$[1,1,1]^{2-}$	$[1,1,1]^{2-}$
—	$[1,1,2]^-$	$[1,1,2]^-$	$[1,1,2]^-$	$[1,1,2]^-$
$[2,2,4]^{2-}$	$[2,2,4]^{2-}$	$[2,2,4]^{2-}$	*	*
$[2,2,5]^-$	$[2,2,5]^-$	$[2,2,5]^-$	*	*
$[2,2,6]^-$	$[2,2,6]^-$	$[2,2,6]^-$	*	*
—	—	$[1,2,1]^{3-}$	$[1,2,1]^{3-}$	$[1,2,1]^{3-}$
—	—	$[1,2,2]^{2-}$	$[1,2,2]^{2-}$	$[1,2,2]^{2-}$
—	—	—	$[2,1,4]^-$	$[2,1,4]^-$
—	—	—	$[2,1,5]^-$	$[2,1,5]^-$
—	—	—	$[4,4,9]^{3-}$	$[4,4,9]^{3-}$
—	—	—	$[4,4,10]^{2-}$	$[4,4,10]^{2-}$
—	—	—	—	$[2,4,8]^-$
4.36	2.87	2.07	1.61	1.44

* Species rejected by program.

**Fig. 2** Concentration of complexes, expressed as a percentage of the total molybdenum concentration, as a function of pH_c for a solution of $0.005 \text{ mol dm}^{-3} \text{ Mo}^{\text{VI}}$ and $0.100 \text{ mol dm}^{-3}$ aspartate

equal concentrations of molybdate and aspartate or even an excess of molybdate, for example $[2,1,4]^-$ and $[2,1,5]^-$. After some extensive model testing we found several different combinations of species which resulted in practically the same fit. For example, alternative models in which either the $[1,1,2]^-$ or $[2,2,4]^{2-}$ species were retained had s values of 2.31 and 2.37 respectively ($s = \text{sample standard deviation}$).⁹ However, using the constants of species obtained in these preliminary models the distribution of the species was subsequently calculated as a function of total concentrations and pH_c to devise experimental conditions that would help to distinguish better between species. Our program KONpH written in fortran for an IBM compatible PC was used for this purpose. Various additional

titrations were then carried out and all the data used in the calculations. The best model obtained comprised nine complexes (Table 1) of which only the $[1,2,1]^{3-}$ was a very minor species ($< 10\%$) under all conditions. In the final computer run two titrations (pertaining to a two- and five-fold excess of ligand respectively) for which the uncomplexed molybdate species were at their highest concentrations were omitted. The fit improved slightly but the model was not affected and practically identical values for the formation constants were obtained. Also, the values calculated for the protonation constants of aspartate were in excellent agreement with those determined independently. The distribution of the various complexes, calculated for a solution with aspartate in twenty-fold excess, is shown in Fig. 2. The major complexes, occurring in relative concentrations greater than 40%, are the $[1,1,1]^{2-}$, $[2,1,4]^-$ and $[2,1,5]^-$.

Except for the $[2,4,8]^-$ species the stoichiometric composition of the other complexes agrees with those of complexes of molybdate with carboxylate¹¹ or α -hydroxy carboxylate¹⁴ ligands reported previously. The $[2,4,8]^-$ complex occurs at low pH_c where the concentration of unprotonated aspartic acid is extremely low and conditions for the formation of dinuclear molybdenum cations $[\text{HMo}_2\text{O}_6]^+$ becomes more favourable. A structure for this complex can therefore be imagined that is related to the dinuclear oxalate complex,^{11,20} $[\text{Mo}_2\text{O}_5(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2]^{2-}$, in which two aspartate ligands are bidentately co-ordinated and the other two monodentately co-ordinated taking the place of the two water molecules, $[\text{Mo}_2\text{O}_5(\text{H}_2\text{L})_2(\text{HL})_2]$. The only species for which the relative standard deviation of the formation constant is greater than 10%, is the $[4,4,10]^{2-}$ with a 23% deviation; for most titrations its concentration was rather small and still on the increase at the lowest pH_c which precludes satisfactory characterization. The identification of the $[1,1,1]^{2-}$ complex is in agreement with the results of previous equilibrium studies^{3,4,8} and a complex with composition $\text{K}_2[\text{MoO}_3\text{L}]\cdot\text{H}_2\text{O}$ has also been isolated in the solid state.⁵ The formation constant $\log \beta_{111} = 6.54$ which converts to the value 16.12 pertaining to unprotonated aspartate, L^{2-} , as the reacting species, can be compared with the values 16.01 ($0.10 \text{ mol dm}^{-3} \text{ NaNO}_3$),⁸ 15.74 ($1.0 \text{ mol dm}^{-3} \text{ NaCl}$, 18°C)⁴ and 16.79 ($0.16 \text{ mol dm}^{-3} \text{ KNO}_3$).³

Except for the $[1,1,1]^{2-}$ complex the reaction model now proposed does not agree with that recently reported,⁸ namely $[1,1,1]^{2-}$, $[2,2,4]^{2-}$, $[2,2,5]^-$ and $[2,2,6]^-$ which pertains to a different ionic medium, *i.e.*, $0.1 \text{ mol dm}^{-3} \text{ NaNO}_3$. This model was based on three potentiometric titrations with molybdate to aspartate ratios of 1:4, 1:5 and 1:10 for an initial molybdate concentration of $2\text{--}3 \times 10^{-3} \text{ mol dm}^{-3}$. For our data pertaining to ionic medium $1.0 \text{ mol dm}^{-3} \text{ NaCl}$ the model now proposed resulted in a much better fit than the model mentioned above ($s = 1.44$ vs. 4.36). The improvement in the fit upon the addition of species to a model comprising initially only four complexes and subsequent rejection of $[2,2,r]$ species is illustrated in Table 2. The final model can be arrived at *via* different routes, for example, by starting with a series of four mononuclear species.

Spectrophotometric Investigation.—For the spectrophotometric titrations a ten- and twenty-fold excess of aspartate (0.1 mol dm^{-3}) over molybdate (0.01 and $0.005 \text{ mol dm}^{-3}$) were used. Under these conditions molybdenum(vi) side equilibria could be neglected as a first approximation. In the case of aspartate in ten-fold excess a maximum of only about 5% of the molybdate is present in the form of heptamolybdates at $\text{pH}_c = 4$. Despite the rather limited wavelength range available for investigating complex formation, the variation in absorption with pH_c at a number of wavelengths shows sufficient variation to be useful for quantitative treatment (Fig. 3).

The two sets of data were treated separately using the program SPECFIT.¹⁰ By application of model-free evolving factor analysis (EFA) concentration profiles for at least four complexes can be constructed. For the data pertaining to

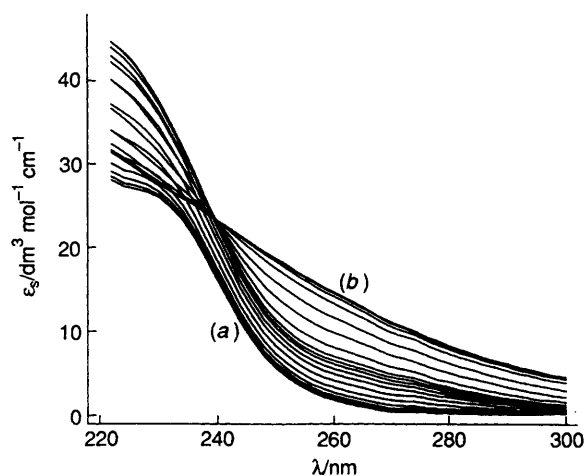


Fig. 3 Change in absorption spectra with pH_c ranging from 6.9 (a) to 2.3 (b); ϵ_s is the molar absorption coefficient of a solution of $0.005 \text{ mol dm}^{-3} \text{ Mo}^{\text{VI}}$ and $0.100 \text{ mol dm}^{-3}$ aspartate

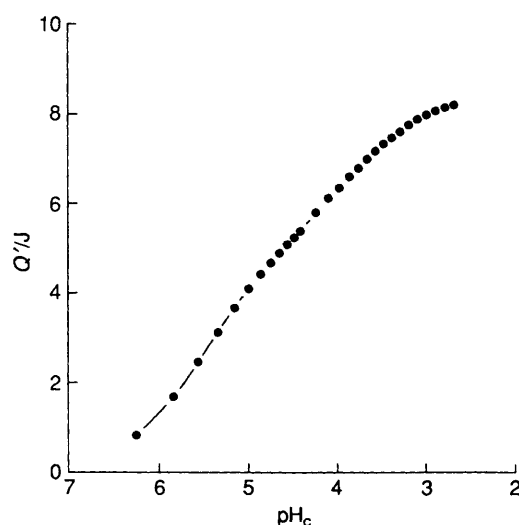


Fig. 4 Heat of complexation, Q' , as a function of calculated pH_c for a titration of a solution of $0.010 \text{ mol dm}^{-3} \text{ Mo}^{\text{VI}}$ and $0.100 \text{ mol dm}^{-3}$ aspartate with $1.0 \text{ mol dm}^{-3} \text{ HCl}$

twenty-fold excess of aspartate, for instance, the concentration profiles show maxima at pH_c 4.8, 3.8 and 3.4 while the concentration of the last component(s) still increases at pH_c 2.3. From the distribution curves shown in Fig. 2 it can be seen that the maxima at pH_c 4.8 and 3.8 correspond with those of the $[1,1,1]^{2-}$ and $[1,2,2]^{2-}$ complexes. Because of the great overlap of equilibria the maximum of the concentration profile at pH_c 3.4 cannot be assigned unambiguously to the $[1,1,2]^{-}$ complex. When EFA is carried out with one more complex the additional concentration profile has a maximum at pH_c 2.9 which concurs approximately with the distribution curve of the $[2,1,4]^{-}$ complex. However, the concentration profile with maximum at pH_c 3.4 is then defined by only one experimental curve. Although this analysis supports the potentiometric results it shows that the change in absorption with pH_c in the measurable wavelength range is not sufficient to evaluate equilibrium constants for all the complexes in the system. Apparently the spectra of some of the species show very little or no change at all in the wavelength range 222–300 nm. Although reasonable values for the formation constants of some of the species could be calculated (while fixing the formation constants of some others) the spectra obtained were most often unsatisfactory with very large or even negative molar absorptivities for some species at certain wavelengths. However, by using only the first ten spectra of each data set (pH_c 7.0–4.9) the formation constant

for the $[1,1,1]^{2-}$ complex could be calculated with the value $\log \beta_{111} = 6.52 \pm 0.02$ (3σ error limits) in very good agreement with that obtained by potentiometry (6.54).

Enthalpimetric Investigation.—The results obtained in a typical enthalpimetric titration of a mixture of molybdate and aspartate with hydrochloric acid is shown in Fig. 4. To present a picture of the heat developed by complex formation alone, the heat evolved by protonation of the free aspartate (in ten-fold excess) has been subtracted from the total measured heat. The curve shows a slight inflexion at $\text{pH}_c \approx 4.8$ where the $[1,1,1]^{2-}$ complex reaches its maximum. At this pH_c about 90% of the molybdate is complexed and the further substantial increase in heat observed with decrease in pH_c implies more favourable enthalpy changes for successive complex formation. This observation is in agreement with a model in which complexes of different structure are successively formed. The enthalpy change involved in the protonation of a complex is usually a relatively small positive or negative quantity.^{11,14}

The enthalpy changes for the formation of the complexes were calculated from the measured heat, Q , corrected for dilution effects, equation (3), where n_{pqr} is the number of moles

$$Q = \sum n_{pqr} \Delta H^{\circ}_{pqr} \quad (3)$$

formed and ΔH°_{pqr} the molar enthalpy change of a given species $[p,q,r]$ at 25°C in $1.0 \text{ mol dm}^{-3} \text{ NaCl}$ medium. The set of linear equations obtained from corresponding Q and n_{pqr} values were solved for the unknown ΔH°_{pqr} parameters using a BMDP least-squares program.²¹ The n_{pqr} values at each titration point were calculated, in a subroutine supplied to the BMDP program, from the concentrations of the species obtained by simultaneous solution of the three mass-balance equations (4)–(6), where b , c and h are the equilibrium

$$B = b + \sum p \beta_{pqr} b^p c^q h^r \quad (4)$$

$$C = c + \sum q \beta_{pqr} b^p c^q h^r \quad (5)$$

$$H = h + \sum r \beta_{pqr} b^p c^q h^r \quad (6)$$

concentrations of $[\text{MoO}_4]^{2-}$, HL^{-} and H^{+} respectively.

The enthalpy changes for the protonation of HL^{-} in $1 \text{ mol dm}^{-3} \text{ NaCl}$, $\Delta H^{\circ}_{011} = -5.8 \text{ kJ mol}^{-1}$ and $\Delta H^{\circ}_{012} = -10.2 \text{ kJ mol}^{-1}$, were determined in separate titrations and treated as fixed parameters in the calculation of the ΔH°_{pqr} values of the complexes. The enthalpy changes for the protonation of aspartate²² can be compared with the literature values of -5.0 and $-13.4 \text{ kJ mol}^{-1}$. The very small amount of heat ($< 3.5\%$ at any titration point) contributed by the side reactions of molybdate with hydrogen ions has also been taken into account in the calculations using known ΔH°_{p0r} values of molybdate species¹⁸ which are present in concentrations ranging from 0.5 to 5%.

Evaluation of reliable ΔH° values for all the species in the pH_c region < 4.0 and especially for the minor species is problematical considering the great overlap of the equilibria. Therefore, rather than neglecting some of the minor species, the quite reasonable approximation, based on results of previous investigations,^{11,14} was made that the enthalpy change for a complex and its protonated form have about the same value. The data were therefore treated on the assumption that $\Delta H^{\circ}_{112} = \Delta H^{\circ}_{111}$ and $\Delta H^{\circ}_{4410} = \Delta H^{\circ}_{449}$. Since ΔH°_{111} could be calculated with sufficient accuracy the approximation only affected the values of ΔH°_{112} , ΔH°_{449} and ΔH°_{4410} . The calculated thermodynamic quantities for the various species are listed in Table 1.

No such thermodynamic quantities for complex formation of aspartic acid or any other amino acids with molybdenum(vi) are available in the literature for comparison. It is of interest, however, to compare the values with those determined for complexes of molybdenum with some carboxylate or α -hydroxy

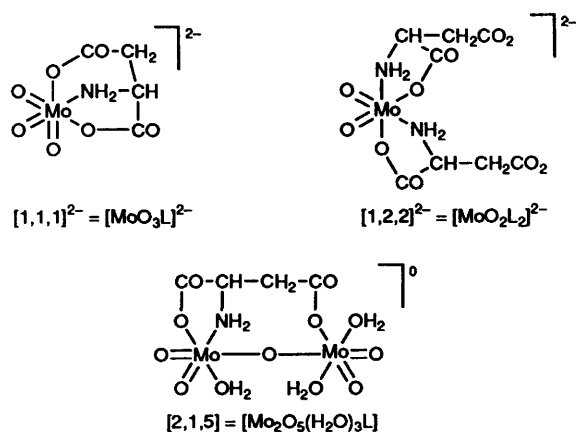


Fig. 5 Proposed structures for some molybdenum(vi)-aspartate complexes

carboxylate ligands.^{1,11,14} For these ligands the enthalpy change for mononuclear complexes of the type $[1,1,r]$ is of the order -50 to -60 kJ mol^{-1} compared to -27 kJ mol^{-1} determined for the $[1,1,1]^{2-}$ aspartate complex. Apparently aspartate co-ordinates with molybdenum *via* the two carboxylate oxygens and nitrogen to form a six- and a five-membered ring respectively.^{4,6} In the case of the $[1,1,2]^{2-}$ oxalate complex, for example, only a five-membered ring is formed. The difference in enthalpy can therefore be attributed to the much weaker bonding of molybdenum(vi) with nitrogen compared to oxygen.

The enthalpy change for the $[1,2,2]^{2-}$ complex is more favourable than that of the $[1,1,1]^{2-}$, but it is still about 30 – 40 kJ mol^{-1} less than that for the $[1,2,r]$ complexes of lactate¹ and tartrate¹⁴ (-70 to -80 kJ mol^{-1}) which again shows the weaker bonding of nitrogen compared to oxygen; it is supposed that the most stable structure for the diaspartate complex is that shown in Fig. 5 in which five-membered rings are formed with nitrogen as one of the donor atoms.

The dinuclear complexes $[2,1,4]^-$ and $[2,1,5]$ have the greatest enthalpy change per molybdenum atom which could indicate that aspartate is co-ordinated to both molybdenum atoms (Fig. 5) resulting in an energetically more favourable utilization of the longer-chain carboxylate group. The main driving force in the complexation of molybdenum(vi) with carboxylate ligands is the favourable enthalpy change emanating from the expansion of the co-ordination sphere of molybdenum from four to six. At $\text{pH}_c < 2.5$ molybdenum species are already six-co-ordinated and little is to be gained by complexation, especially if one of the donor groups is weaker than oxygen. The enthalpy change for the dinuclear cation,¹⁷ $[\text{Mo}_2\text{O}_5(\text{OH})(\text{H}_2\text{O})_5]^+$, is about -90 kJ mol^{-1} compared¹⁸ to -96 and -83 kJ mol^{-1} now determined for the $[2,1,4]^-$ and $[2,1,5]$ complexes respectively. In view of the uncertainties in the ΔH values of the other complexes, $[2,4,8]$, $[4,4,9]^{3-}$ and $[4,4,10]^{2-}$, no further discussion is justified except for noting that the enthalpy change for the $[2,4,8]$ complex is comparatively small while those for the tetranuclear complexes appear to be of the correct order of magnitude namely about -31 kJ mol^{-1} per molybdenum atom.

Conclusion

The results of this investigation show that complex formation between molybdenum(vi) and aspartate is not particularly

strong and that a ten-fold excess of ligand is needed to complex more than 90% of the molybdenum. The co-ordinating characteristics of the ligand are such that a number of minor species occur in greatly overlapping equilibria. Characterization of these complexes is therefore difficult and the model might to some extent depend upon the conditions employed. The following major complexes have been identified: $[\text{MoO}_3\text{L}]^{2-}$, $[\text{MoO}_2\text{L}_2]^{2-}$, $[\text{Mo}_2\text{O}_5(\text{OH})(\text{H}_2\text{O})_2\text{L}]^-$ and $[\text{Mo}_2\text{O}_5(\text{H}_2\text{O})_3\text{L}]$ of which the first one is the most important and reaches its maximum concentration at $\text{pH}_c = 4.8$; the formulae are based on the structures proposed in Fig. 5. The thermodynamic quantities determined for the complexes show that the weaker donor properties of aspartate towards molybdenum compared to those of oxalate and lactate, for example, are enthalpy related and due to weak binding between nitrogen and molybdenum in aqueous solution.

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