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MOLYBDENUM(VI) COMPLEX FORMATION—8. EQUILIBRIA AND THERMODYNAMIC QUANTITIES FOR THE REACTIONS WITH CITRATE

J. J. CRUYWAGEN,* E. A. ROHWER and G. F. S. WESSELS

Department of Chemistry, University of Stellenbosch, Stellenbosch 7600, South Africa

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Abstract—Complex formation between molybdate and citrate has been investigated in the pH range 1.0–9.0 by potentiometry, spectrophotometry, differential pulse polarography and calorimetry in NaCl (1.0 mol dm^{-3}). The "best" reaction model comprises mononuclear, dinuclear and tetranuclear complexes. 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 $[(MoO_4)_p(cit)_qH_r]^{(2p+3q-r)-}$, have the values (at 25°C): $\log \beta_{111} = 8.35$, $\log \beta_{112} = 15.00$, $\log \beta_{113} = 19.62$, $\log \beta_{114} = 21.12$, $\log \beta_{224} = 31.02$, $\log \beta_{225} = 35.86$, $\log \beta_{226} = 40.08$, $\log \beta_{124} = 25.34$, $\log \beta_{125} = 29.54$, $\log \beta_{126} = 33.34$, $\log \beta_{213} = 21.73$, $\log \beta_{214} = 26.90$, $\log \beta_{215} = 31.53$, $\log \beta_{429} = 60.76$, $\log \beta_{4210} = 64.69$ and $\log \beta_{4411} = 77.45$. A set of stability constants pertaining to 2°C has also been determined. These constants were used to calculate species distribution curves needed to evaluate the differential pulse polarographic data obtained at 2°C. The polarographic results were consistent with the reaction model derived from the potentiometric data. Enthalpy and entropy changes for complexes occurring in sufficiently high concentrations were calculated from the calorimetric data. The enthalpy changes are as follows: $\Delta H^0_{111} = -48.5$, $\Delta H^0_{112} = -55.6$, $\Delta H^0_{113} = -66.5$, $\Delta H^0_{114} = -69$, $\Delta H^0_{224} = -140$, $\Delta H^0_{225} = -137$, $\Delta H^0_{226} = -142$, $\Delta H^0_{126} = -92$, $\Delta H^0_{214} = -117$, $\Delta H^0_{215} = -117$, $\Delta H^0_{4210} = -251$ and $\Delta H^0_{4411} = -305$ kJ mol^{-1}. Approximate values for the following enthalpy changes were calculated from the two sets of constants determined at 25 and 2°C: $\Delta H^0_{124} = -77$, $\Delta H^0_{125} = -83$, $\Delta H^0_{213} = -81$ and $\Delta H^0_{429} = -252$ kJ mol^{-1}.

Equilibrium constants and thermodynamic parameters for the formation of some molybdenum(VI) citrate complexes have been reported for the first time in a previous paper.[1] A series of mononuclear complexes, represented for brevity by the stoichiometric coefficients of the reactants, molybdate, citrate and protons, i.e. $[1,1,1]^{4-}$, $[1,1,2]^{3-}$ and $[1,1,3]^{2-}$ as well as two dinuclear complexes, namely, $[2,1,4]^{3-}$ and $[2,1,5]^{2-}$, have been characterized. Subsequently, similar investigations have been conducted of the complexation of various other carboxylate ligands with molybdenum(VI) and also with tungsten(VI).[2–4] The results of these and other studies showed that, depending on the conditions and the nature of the ligand, several complexes of certain typical stoichiometries (including those mentioned above) can be identified in solution and in some cases isolated in the solid state.[5] For instance, complexes of the composition $[1,2,r]$ are quite typical for an α-hydroxycarboxylic acid as a ligand.[3,6] Also, the stoichiometry $[2,2,r]$ appears to be quite common and has been reported for complexes of oxalate,[7,8] malate[9] and nitrilotriacetate[2,10] with molybdenum. Recently, two dinuclear compounds, $K_6[Mo_2O_5(cit)_2]\cdot 7H_2O$ and $K_4[Mo_2O_5(Hcit)_2]\cdot 5H_2O$, have been obtained by precipitation from aqueous solution; these complexes have been characterized by a variety of methods.[11] In the case of tungsten(VI) a dinuclear citrate complex, $Na_6[W_2O_5(cit)_2]\cdot 10\ H_2O$ has been

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*Author to whom correspondence should be addressed.

structurally characterized by X-ray analysis.[12] The structures of tetranuclear complexes of molybdenum(VI) with malate[13] and citrate,[14] namely $[Mo_4O_{11}(mal)_2]^{4-}$ and $[Mo_4O_{11}(Hcit)_2]^{4-}$ have been determined by single-crystal X-ray analysis.

In view of these new findings it seemed worthwhile to extend our previous investigation of the molybdenum(VI) citrate system, covering wider pH and concentration ranges, in an attempt to characterize all possible complexes in terms of equilibrium constants and thermodynamic parameters. Such information would be of special value for the interpretation of data obtained by other experimental techniques, in particular calorimetry[1–4] and also NMR spectroscopy which has often been successfully applied to obtain structural information of complexes of this type.[15]

In this investigation the identification of the various complexes was based mainly on potentiometric data which were treated with the program SUPERQUAD.[16] The formation constants thus determined were used for the interpretation and treatment of calorimetric data to extract the required enthalpy and entropy changes for complexation. Due to the complexity of the system the application of spectrophotometry is rather limited, but the results obtained were consistent with those obtained by potentiometry.

For investigations of this nature and especially when the reaction model comprises many species there is a need for an additional method to check the validity of the reaction model. In the present study differential pulse polarography was used for the first time in a semi-quantitative way to fulfil this purpose. Most of the polarographic methods for the determination of molybdenum(VI) are based on the reduction of a complexed species with the ligand, quite often a hydroxycarboxylic acid such as lactic, malic or citric acid, in large excess.[17] The polarographic reduction of molybdenum(VI) in the presence of citric acid has been investigated by several authors, but the interpretation of the results has been hampered by a lack of knowledge about the identity and stability regions of the electroactive complex species, as well as that of the reduced products.[18,19] The most recent study of the polarographic behaviour of molybdenum in citrate medium showed that a very low temperature (2°C) is required if the limiting current is to be controlled entirely by diffusion of the electroactive complex from the bulk solution.[19] By taking advantage of this effect the $[1,1,1]^{4-}$ complex could be identified and an approximate constant for its formation in slightly alkaline solution was determined. For the present investigation the method of differential pulse polarography was chosen because of its sensitivity and very favourable signal-to-noise ratio; in fact, it is rapidly replacing classical polarography in many laboratories.[20] A differential pulse polarogram shows a peak at a voltage corresponding to the half-wave potential in an ordinary d.c. polarogram and the peak height is proportional to the concentration of the reduced species. It is clear therefore that this technique would have great potential as a complementary model—checking method by indicating the occurrence of reducible complexes which can be correlated with known concentrations of species in solution.

EXPERIMENTAL

Reagents and solutions

All reagents were of analytical grade (Merck, BDH and Aldrich) and solutions were prepared with water obtained from a Millipore Milli-Q system. Sodium molybdate stock solution was prepared from the recrystallized salt $Na_2MoO_4 \cdot 2H_2O$ and standardized gravimetrically as described previously.[2] Sodium citrate was used as received. The purity of the salt (99.9%) was verified by refinement of the concentration of a solution (0.02 M) using the program SUPERQUAD[16] to calculate the protonation constants of citrate from the data of a potentiometric titration with hydrochloric acid (0.25 M). Hydrochloric acid was standardized indirectly against potassium hydrogenphthalate by titration with sodium hydroxide. Sodium chloride was purified as described previously.[2]

Potentiometric titrations

Mixtures of sodium molybdate and sodium citrate were titrated with hydrochloric acid at 25°C using a Metrohm 636 Titroprocessor. All solutions were made 1.0 M 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 NaCl (1.0 M) and then bubbled slowly through the titration solution. The initial concentrations (mol dm^{-3}) of molybdate and citrate were as follows: 0.01, 0.04; 0.05, 0.10; 0.01, 0.01; 0.05, 0.05; 0.1, 0.1 and 0.02, 0.01, thus obtaining solutions with equal concentrations of molybdate and citrate or an excess of one of these reactants; the pH_c range covered was 9.0–1.0. As a rule titrations were carried out in duplicate, but only 600 data points (maximum allowed by the program) were used in the calculations.

The free hydrogen ion concentration, h, was determined by measuring the potential, E^0, to ± 0.2

mV using a Ross combination electrode (Orion) with a 3.0 M KCl bridge solution. Eq. (1) was used to calculate h from the measured potential at each titration point:

$$E = E^0 + 0.1985T\log h + E_j \qquad (1)$$

where T denotes the temperature in Kelvin. Values for E^0 and E_j were determined from titrations of 1.0 M NaCl with HCl as described by Rossotti.[21] For brevity $-\log h$ is denoted by pH_c.

A series of potentiometric titrations, similar to those described above for 25°C, have also been carried out at 2°C. Appropriate values for E^0 and E_j were determined in the same way and substituted in eq. (1) for the calculation of h. The initial concentrations (mol dm^{-3}) of molybdate and citrate in these experiments were as follows: 0.01, 0.01; 0.05, 0.05; 0.1, 0.1; 0.005, 0.01; 0.01, 0.02; 0.05, 0.1; 0.01, 0.005 and 0.02, 0.01, thus obtaining solutions with equal concentrations of molybdate and citrate or an excess of one of these reactants. Again all titrations were performed in duplicate and 600 data points were used in the calculations. A citrate solution (0.02 M) was titrated with hydrochloric acid (1.0 M) in order to determine the protonation constants of citrate at 2°C.

Spectrophotometric titrations

A Varian Cary 210 spectrophotometer in conjunction with an Apple IIe computer was used for absorption measurements and data collection. Cuvette holders were water-jacketed to maintain the temperature at 25°C by circulation of water from a thermostat. The ionic medium was 1.0 M NaCl and the absorbances were measured against 1.0 M NaCl solution in the wavelength range 206–320 nm using quartz cuvettes of path length 1.0 cm. The concentrations of molybdate and citrate in the reaction vessel (kept in a waterbath at 25°C) were 1.0×10^{-4} and 1.2×10^{-4} M, respectively. The titrant solution contained in addition to hydrochloric acid (0.025 M) also molybdate and citrate at the same concentration as the test solution. The hydrogen ion concentration was measured as described for the potentiometric titrations. 24 Spectra were recorded at pH_c intervals of 0.1–0.25 in the range 5.6–1.0. A similar titration of citrate (0.0016 M) with hydrochloric acid (0.25 M) was carried out to record 19 spectra from which the individual spectra of the various citrate species were calculated using the program SPECFIT.[22] These spectra were supplied to the program SQUAD[23] for the treatment of the absorption data pertaining to complexation. In the wavelength range used the absorption of citrate species is very small compared with that of molybdate.

Differential pulse polarography

Differential pulse polarograms were recorded using a Metrohm Polarecord E506 with an E505 polarographic stand. A thermostatted Metrohm cell with a three-electrode system was used: a dropping mercury electrode with a drop time of 0.4 s at 86.2 cm mercury height as the working electrode, a silver–silver chloride (3 M KCl) reference electrode and a platinum wire auxiliary electrode. The solutions were deaerated with purified nitrogen for at least 30 min before polarograms were recorded at 2°C. The scan rate was 5 mV s^{-1} and the pulse amplitude 52 mV.

Calorimetric titrations

An isothermal calorimeter, Tronac model 1250, was used for the enthalpy measurements. Solutions containing molybdate and citrate (20.0 cm^3) were titrated with hydrochloric acid from a precision microburette (2.5 cm^3). The data were collected automatically by means of a personal computer using software supplied by Tronac. The initial concentrations of equimolar solutions of molybdate and citrate were 0.01, 0.04 and 0.05 M. Again, all solutions were made 1.0 M with respect to chloride by the addition of the appropriate amount of recrystallized sodium chloride. The titrations were carried out in duplicate and the pH_c covered was 8.0–1.5. The data were corrected for the endothermic heat of dilution of hydrochloric acid titrated into sodium chloride by using results of previous blank titrations.[24]

RESULTS AND DISCUSSION

Potentiometric investigation

The various protonation, condensation and complexation reactions that can take place when a solution containing molybdate and citrate is acidified are represented by the general eq. (2).

$$p\mathrm{MoO_4^{2-}} + q\mathrm{Hcit^{3-}} + r\mathrm{H^+} \rightleftharpoons [\mathrm{COMPLEX}]^{(2p+3q-r)-} \qquad (2)$$

The citrate anion is formulated as $Hcit^{3-}$ to show the proton of the α-hydroxyl group, which is released only when complexation takes place. For brevity, species with overall formation constants $\beta_{p,q,r}$ will mostly be described by the stoichiometric coefficients defining their composition, for example $[1,1,1]^{4-}$ for the complex $[MoO_3(cit)]^{4-}$.

The results of some representative titrations of citrate and of mixtures of molybdate and citrate with hydrochloric acid are shown in Fig. 1. as plots of F against pH_c. The function F [eq. (3)] represents the fraction of the total negative charge neutralized due to protonation, where H, B, and C are the analytical concentrations of acid, molybdate and citrate, respectively:

$$F = (H-h)/(2B+3C). \tag{3}$$

An F value of 1.0 would therefore indicate an average charge of zero for the species in solution. For a solution containing only citrate species this is the case at *ca* pH 1 where H_4cit is the major component (Fig. 1). Complex formation results in lower F values, e.g. from 0.7 to 0.8 at *ca* pH 1, as is observed for solutions of equal concentrations of citrate and molybdate; these F values correspond to complexes having stoichiometries such as 2 : 1 : 5 and 1 : 1 : 4 for molybdate : citrate : protons.

At high pH, on the other hand, the effect of complex formation is clearly seen in the much greater F values for solutions of mixtures of molybdate and citrate compared with that of a citrate solution alone. The inflexions of the curves pertaining to an excess of either molybdate or citrate only reflect the difference in basicity of the complexes on the one hand and that of the free molybdate and citrate species on the other.

The inflexions exhibited by the F vs. pH curves for solutions of equal concentrations of molybdate and citrate indicate the presence of major complexes. Thus, stoichiometries of 1 : 1 : 2 and 1 : 1 : 3 are indicated by F values of 0.4 and 0.6 at pH 5.5 and 3.5, respectively (cf. species distribution curves Fig. 2).

Due to the excess of either molybdate or citrate employed in some titrations, side-reactions of protons with uncomplexed molybdate and citrate were taken into account in the treatment of the data. The molybdate species $[HMoO_4]^-$, $[MoO_3(OH_2)_3]$, $[MoO_2(OH)(OH_2)_3]^+$, $[HMo_2O_7]^-$, $[Mo_7O_{24}]^{6-}$, $[HMo_7O_{24}]^{5-}$, $[H_2Mo_7O_{24}]^{4-}$, $[H_3Mo_7O_{24}]^{3-}$, $[Mo_8O_{26}]^{4-}$ and $[HMo_2O_6]^+$ were taken into account using previously determined equilibrium constants pertaining to 1.0 M NaCl medium at 25°C.[25–27] Due to the formation of complexes having a 2 : 1 or 4 : 2 molybdate to citrate stoichiometry at pH < 3, the amount of uncomplexed molybdate is so small that the concentrations of some of the polyoxomolybdate ions, e.g. $[H_3Mo_7O_{24}]^{3-}$ and $[Mo_8O_{26}]^{4-}$, could be neglected in the final calculations. Values for the formation constants of molybdate species required to treat the data collected at 2°C were estimated by using known ΔH values.[27] Previously reported protonation constants of citrate[1] pertaining to 25°C and 1.0 M NaCl have been utilized, but values at 2°C were determined in separate titrations.

The calculation of stability constants and model testing were performed with the computer program SUPERQUAD.[16] The program automatically

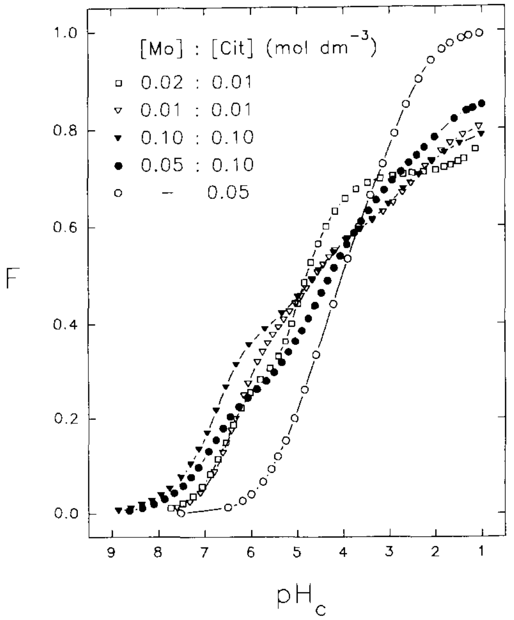


Fig. 1. Plots of function F vs. pH_c for some representative potentiometric titrations.

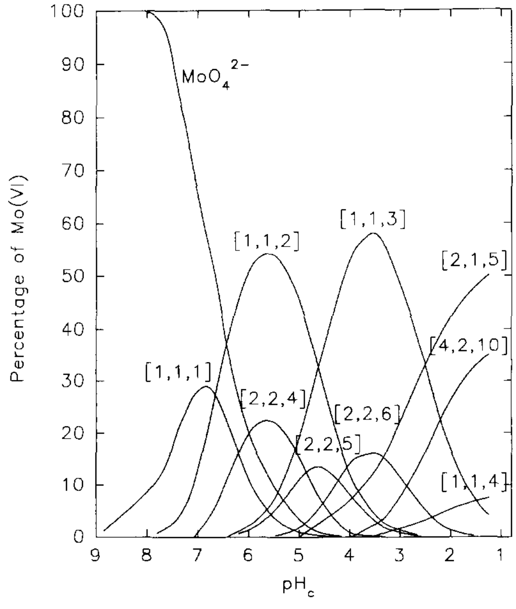


Fig. 2. Distribution of species in the molybdenum(VI) citrate system as a function of pH_c for an equimolar solution of 0.04 M.

rejects species for which the relative standard deviation of the formation constant is greater than 33% (or $3\sigma > 0.43$ log units). The reaction model obtained after considering all possible species (in various combinations) with $p = 1$–4 and having reasonable q and r values is listed in Table 1. The results for the two temperatures differ only with respect to some of the minor complexes: the relatively large tetranuclear complexes $[4,2,8]^{6-}$ and $[4,4,12]^{8-}$ apparently only occur in the solutions pertaining to 2°C, whereas the smaller $[1,1,4]^{-}$ and $[2,1,4]^{3-}$ are found only at 25°C. The molybdenum:citrate stoichiometry of the complexes are typical of those previously observed for comparable molybdenum–ligand systems. The relative standard deviations of the formation constants for the $[4,4,11]^{9-}$ and $[4,4,12]^{8-}$ complexes are 14 and 24%, respectively, for the data pertaining to 2°C. For the data at 25°C the relative standard deviation for the $[4,4,11]^{9-}$ complex is 17%. Although these deviations are significantly greater than those for most other complexes, they are well within the rejection limit of 33%. Therefore, although evidence for the existence of the $[4,4,11]^{9-}$ and $[4,4,12]^{8-}$ complexes is not particularly strong, the complete model together with values for stability constants are listed in Table 1.

The isolation of molybdenum(VI) citrate complexes in crystalline form suitable for X-ray structural analysis has proven to be quite difficult and only one of the complex ions now identified in solution, i.e. $[4,2,10]^{4-}$, has been crystallographically characterized.[14] The potassium salts of the $[1,1,1]^{4-}$, $[2,2,4]^{6-}$ and $[2,2,6]^{4-}$ complexes have been isolated in the solid state, but were characterized by chemical analysis and various other methods.[11] A complex of composition $M_2[Mo_2O_5(OH)H_2O(Hcit)]\cdot 0.5\ H_2O$, where M is K^+ or NH_4^+, and which corresponds to $[2,1,5]^{2-}$, has also been reported.[28] Recently the first X-ray crystallographic analysis of a tungsten citrate complex, $Na_6[W_2O_5(cit)_2]\cdot 10H_2O$, has been reported.[12] The stoichiometry of this complex is similar to that of the $[2,2,4]^{6-}$ ion now identified

Table 1. Values of the formation constants and other thermodynamic quantities (kJ mol^{-1}) for molybdenum(VI) citrate complexes and some tungsten(VI) citrate complexes in 1 M NaCl

Complex $[p,q,r]$	$\log\beta \pm 3\sigma$ (25°C)	$\log\beta \pm 3\sigma$ (2°C)	ΔG^0 (25°C)	ΔH^0 (25°C)	$T\Delta S^0$ (25°C)	ΔH_{temp}
$[0,1,1]^{2-}$	5.12±0.01	5.14±0.01	−29.2	−1.3	28	−1.4
$[0,1,2]^{-}$	9.17±0.01	9.27±0.01	−52.4	−5.8	47	−6.9
$[0,1,3]$	11.94±0.02	12.10±0.02	−68.2	−10.1	58	−11.1
$[1,1,1]^{4-}$	8.35±0.01	9.10±0.01	−47.7	−48.5±0.5	−1	−51±3
$[1,1,2]^{3-}$	15.00±0.01	15.78±0.02	−85.6	−55.6±0.5	30	−53±3
$[1,1,3]^{2-}$	19.62±0.01	20.56±0.03	−112.0	−66.5±1.6	46	−64±3
$[1,1,4]^{-}$	21.12±0.11	—	−120.5	−69±3	52	—
$[2,2,4]^{6-}$	31.02±0.03	33.08±0.03	−177.1	−140±4	37	−141±4
$[2,2,5]^{5-}$	35.86±0.05	37.99±0.04	−204.7	−137±4	68	−146±6
$[2,2,6]^{4-}$	40.08±0.07	42.15±0.17	−228.8	−142±8	87	−142±17
$[1,2,4]^{4-}$	25.34±0.18	26.46±0.15	−144.6	—	—	−77±23
$[1,2,5]^{3-}$	29.54±0.11	30.75±0.10	−168.6	—	—	−83±15
$[1,2,6]^{2-}$	33.34±0.02	34.74±0.02	−190.3	−92±8	98	−96±3
$[2,1,3]^{4-}$	21.73±0.09	22.92±0.17	−124.0	—	—	−81±18
$[2,1,4]^{3-}$	26.90±0.06	—	−153.5	−117±8	37	—
$[2,1,5]^{2-}$	31.53±0.03	33.32±0.05	−180.0	−117±8	63	−122±6
$[4,2,8]^{6-}$	—	59.76±0.11	—	—	—	—
$[4,2,9]^{5-}$	60.76±0.15	64.45±0.15	−346.8	—	—	−252±21
$[4,2,10]^{4-}$	64.69±0.11	68.39±0.10	−369.2	−251±8	118	−253±15
$[4,4,11]^{9-}$	77.45±0.24	81.67±0.20	−442.1	−305±20	137	−289±31
$[4,4,12]^{8-}$	—	85.72±0.36	—	—		—
Tungsten(VI)						
$[1,1,1]^{4-}$	10.21±0.01		−58.3	−66±1	−7	
$[1,1,2]^{3-}$	17.03±0.01		−97.2	−67±3	30	
$[1,1,3]^{2-}$	21.67±0.01		−123.7	−78±1	46	
$[1,1,4]^{-}$	22.82±0.03		−130.2	−82±6	48	

ΔH_{temp} = enthalpy deduced from the change in formation constants with temperature.

in the molybdenum citrate system. In fact, all the tungsten citrate complexes characterized in a recent potentiometric study[4] have molybdenum analogues. In the case of the tungstate system, fewer complexes can be identified because of restrictions on experimental conditions necessitated by the occurrence of slow polyanion equilibria.

The values of the formation constants show that the tungsten citrate complexes are significantly more stable than the molybdenum citrate complexes (Table 1). For example, the difference between the respective stability constants is *ca* 2 log units in the case of the $[1,1,r]^{(5-r)-}$ series. However, the values of the successive protonation constants of these complexes are very similar, e.g. 6.65, 4.62 and 1.50 for molybdenum compared with 6.82, 4.64 and 1.11 for tungsten. Similar trends apply to the lactate complexes of these elements.[3]

The formation constants now determined for the $[1,1,1]^{4-}$, $[1,1,2]^{3-}$, $[1,1,3]^{2-}$, $[2,1,4]^{3-}$ and $[2,1,5]^{2-}$ complexes can be compared with values previously obtained in a less comprehensive investigation: log $\beta_{111} = 8.35$ (8.25), log $\beta_{112} = 15.00$ (15.08), log $\beta_{113} = 19.62$ (19.66), log $\beta_{214} = 26.90$ (27.27) and log $\beta_{215} = 31.53$ (31.86); the values in parentheses refer to the previous investigation.[1]

Spectrophotometric investigation

The complexation reactions were investigated by measuring the change in absorption of molybdate with pH_c in the UV region. Due to the complexity of the system, independent characterization of the complexes by spectrophotometry is not possible. However, conditions could be chosen for which all complexes except $[1,1,2]^{3-}$, $[1,1,3]^{2-}$ and $[2,1,5]^{2-}$ can be neglected, thereby bringing about a considerable simplification. Even so, it has been necessary to use results obtained from other experiments in the final treatment of the data in order to extract the desired information.

At the rather low molybdate concentration required for the absorption measurements, a slight excess of citrate is essential to promote complex formation, especially at $pH_c < 5$, where the formation of protonated and condensed molybdate species must be counteracted. The absorption of uncomplexed citrate species, though much smaller than that of molybdate, must therefore be taken into account. A separate spectrophotometric titration was carried out from which the absorption spectra as well as the protonation constants for the various citrate species were calculated with the program SPECFIT.[22] These spectra are shown in Fig. 3 from which it is seen that successive protonation of citrate causes a consistent decrease in the absorption of the resulting species at wavelengths below *ca* 215 nm. The values obtained for the protonation constants, namely log $\beta_{011} = 5.09$ (5.12), log $\beta_{012} = 9.13$ (9.17) and log $\beta_{013} = 11.95$ (11.94), are in excellent agreement with values (in parentheses) previously calculated from potentiometric data pertaining to the same ionic medium.[1]

Below *ca* pH_c 2.5 not all molybdate is complexed under the conditions employed. Previously determined absorption spectra and formation constants of the mononuclear species $[MoO_3(OH_2)_3]$ and $[MoO_2(OH)(OH_2)_3]^+$ were therefore supplied as "knowns" in the treatment of the data. However, to check for consistency the spectrum of either of these two species was calculated in some of the runs. The spectra thus obtained agreed very well with those previously determined.[29]

Although complex formation causes a change in the spectrum (Fig. 4), which can be used for mathematical treatment, it turned out that the difference between the absorption of the two mononuclear complexes in particular is very small. Owing to the large number of wavelengths used this difference proved to be sufficient for the determination of the formation constants mainly because protonation of the $[1,1,2]^{3-}$ complex results in a simultaneous decrease (below 250 nm) and increase (above 260 nm) in absorption, albeit rather small. The values calculated for the formation constants, log $\beta_{112} = 14.99$ (15.00), log $\beta_{113} = 19.67$ (19.62) and log $\beta_{215} = 31.77$ (31.53), agree surprisingly well with those (in parentheses) determined by potentiometry. Characterization of the other complexes by spectrophotometry was not attempted because of the large number of equilibria (and spectra) to be considered for a relatively small change in absorption with pH_c.

Differential pulse polarographic investigation

A noticeable feature of the molybdenum(VI) citrate complexes is the variety of structural types

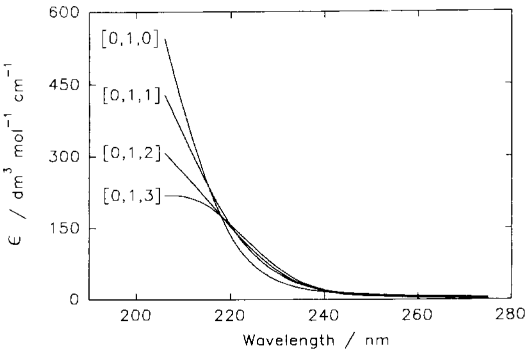


Fig. 3. Calculated molar absorption spectra of the various citrate species.

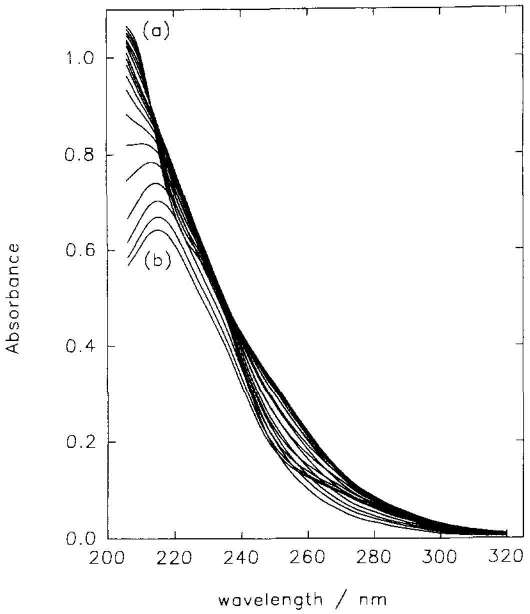


Fig. 4. Change in absorption spectra with pH_c ranging from (a) $pH_c = 5.6$ to (b) $pH_c = 1.0$. $[Mo^{VI}] = 0.0001$ M, [cit] = 0.00012 M.

which occur in accordance with the various molybdenum : citrate stoichiometries, namely 1 : 1, 2 : 2, 4 : 4, 1 : 2, 2 : 1 and 4 : 2. This attribute is a direct consequence of the coordination capacity of citrate and the general behaviour of molybdenum(VI) in complexing α-hydroxycarboxylates. Since these structural differences should affect the redox behaviour of the complexes, an investigation by differential pulse polarography (DPP) can be expected to provide some independent evidence in support of the proposed reaction model.

Molybdenum(VI) can be reduced to various lower oxidation states, but mixed-valence species are also found in aqueous solutions. Several of these lower valent cationic species have been identified,[30] e.g. the stable dinuclear Mo^V cation, $[Mo_2O_4(H_2O)_6]^{2+}$, the Mo^{IV} trinuclear cation, $[Mo_3O_4(H_2O)_9]^{4+}$, the Mo^{III} cations of varying nuclearity, namely $[Mo(H_2O)_6]^{3+}$, $[Mo_2(OH)_2(H_2O)_8]^{4+}$ and $[Mo_3(OH)_4]^{5+}$, and the dinuclear Mo^{II} cation, $[Mo_2(H_2O)_8]^{4+}$. This plethora of reduction products, further compounded by various possible complexation reactions with citrate, renders the polarographic behaviour of molybdenum(VI) quite complex. The DPP experiments should therefore be regarded as exploratory in the sense of using it as a crude model-checking device rather than as a method to explain the polarographic behaviour of molybdenum(VI) in the presence of citrate ions.

In their investigation of the polarographic reduction of molybdenum(VI) in the presence of citrate at ca pH 8.2, Creager *et al.*[19] have shown that a very low temperature is required to suppress the kinetic portion of the limiting current. At 2°C the rate of formation of the electroactive Mo^{VI} citrate species is so small that on the polarographic time-scale the limiting current is controlled virtually entirely by diffusion of the complex from the bulk solution. By using the proportionality between the limiting current and the concentration of the electroactive species these authors could deduce an approximate value for the formation constant of the $[1,1,1]^{4-}$ complex (log β *ca* 8.4), which agrees reasonably well with the value determined in the present investigation, i.e. log $\beta_{111} = 9.1$. For the purpose of the present investigation it has been assumed that the limiting current is diffusion controlled at all potentials and under all conditions. Most of the differential pulse polarograms were therefore recorded at 2°C and the results examined in terms of the postulated reaction model and species distribution curves pertaining to 2°C.

A differential pulse polarogram of a molybdenum citrate solution (1 mM molybdate + 100 mM citrate) at $pH_c = 8.9$, shows a strong reduction peak at -1.78 V and a much weaker peak at -1.25 V (Fig. 5). Only the $[1,1,1]^{4-}$ complex occurs in significant amounts in this solution (13.5% of the molybdenum is complexed) and the two peaks can therefore be associated with the stepwise reduction of this complex to form two lower oxidation states of molybdenum(VI). When the pH_c is lowered to 7.2, the polarogram shows an increase in the peak currents due to the increase in the percentage concentration of the $[1,1,1]^{4-}$ complex from 13.5 to 69.4%. However, at this pH the protonated form of the $[1,1,1]^{4-}$ complex, namely the $[1,1,2]^{3-}$ species, also occurs in the solution at a concentration of 21.2%, which explains the appearance of a new peak at -1.1 V.

A fourth reduction peak occurs at -0.85 V when the concentration of the $[1,1,3]^{2-}$ complex reaches a sufficient level; for example, a polarogram at pH = 5.5 of a 1 mM molybdate solution containing only a 10-fold excess of citrate (to limit the relative concentration of $[1,2,r]$ complexes to less than 2%) shows this peak in addition to those mentioned above. Under these conditions the two mononuclear complexes $[1,1,2]^{3-}$ and $[1,1,3]^{2-}$ are the major components in the solution.

The appearance and growth of the four peaks at potentials -1.78, -1.25, -1.1 and -0.85 V therefore serve well to verify the existence of the three $[1,1,r]$ complexes. However, the peak heights do not necessarily correlate with the concentrations of the individual complexes *over the whole* pH_c *range*. For example, the height of the reduction peak at -1.78 V is not determined only by the concentration of $[1,1,1]^{4-}$ complex, but also by the $[1,1,2]^{3-}$ and $[1,1,3]^{2-}$ complexes in keeping with their formation with decreasing pH_c. This can be inferred from the curves in Fig. 6, where both the distribution of these species and the peak current are plotted as a function of pH_c.

This behaviour can be understood in terms of the stepwise reduction of molybdenum(VI) to lower oxidation states. The first reduction step of the $[1,1,r]$ complexes occurs at increasingly lower negative potential with successive protonation, namely -1.25, -1.05 and -0.85 V for the $[1,1,1]^{4-}$, $[1,1,2]^{3-}$ and $[1,1,3]^{2-}$ complexes, respectively. Further reduction to the next oxidation state seems to be less dependent on the degree of protonation of the complexes and then takes place, for all complexed molybdenum, at -1.78 V; the greatest contribution to the peak current comes from the $[1,1,2]^{3-}$ complex (Fig. 6). Therefore, although the $[1,1,1]^{4-}$ complex would not be present at low pH_c, the second step in the reduction of the $[1,1,2]^{3-}$ and $[1,1,3]^{2-}$ complexes accounts for the peak current at -1.78 V.

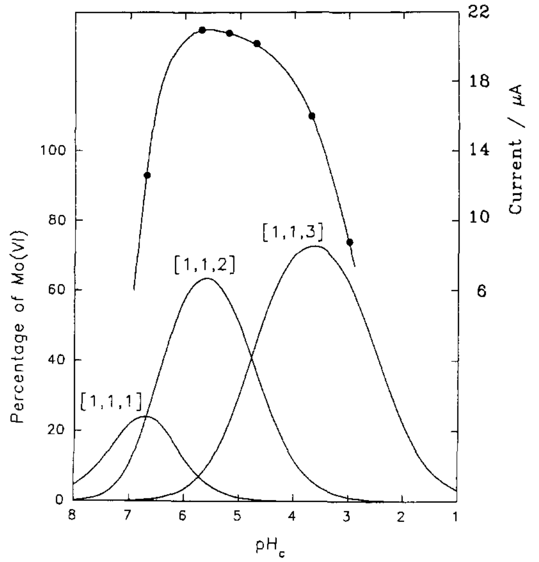


Fig. 6. Peak currents ($E = -1.78$ V) obtained from differential pulse polarograms at various pH_c values for an equimolar solution of molybdate and citrate (0.004 M) compared with the percentage of the monomeric complexes.

The redox behaviour of the dinuclear complexes is expected to be different from that of the mononuclear complexes. This is indeed what is observed. Solutions containing $[2,2,r]$ complexes in addition to the $[1,1,r]$ complexes have polarograms with two extra peaks at -1.48 and -0.5 V. The differential pulse polarograms of an equimolar solution of molybdate and citrate (0.004 M) at different pH_c values in the range 6.7–4.7 are shown in Fig. 7 and can be compared with the species distribution diagram in Fig. 8. The polarogram pertaining to $pH_c = 6.7$ shows the peaks at -1.78, -1.25 and -1.05 V associated with the $[1,1,1]^{4-}$ and $[1,1,2]^{3-}$ complexes, which are the predominant complexes at this pH_c. At $pH_c = 5.7$ both the $[1,1,3]^{2-}$ and $[2,2,4]^{6-}$ complexes also occur in the solution and in addition to the reduction peak of the $[1,1,3]^{2-}$ complex at -0.85 V the two new peaks associated with the dinuclear complex at -1.48 and -0.5 V can be seen on the polarogram.

Further evidence for the assignment of the peaks at -1.48 and -0.5 V to the reduction of dinuclear complexes is obtained by comparing the polarograms of equimolar solutions of molybdate and citrate, 0.004 and 0.008 M at the same $pH_c = 5.7$ (Fig. 9). Doubling of the concentrations has the effect of increasing the concentrations of the dimeric complexes $[2,2,4]^{6-}$ and $[2,2,5]^{5-}$ by a factor of 3.4; while the ratio of their concentrations remains

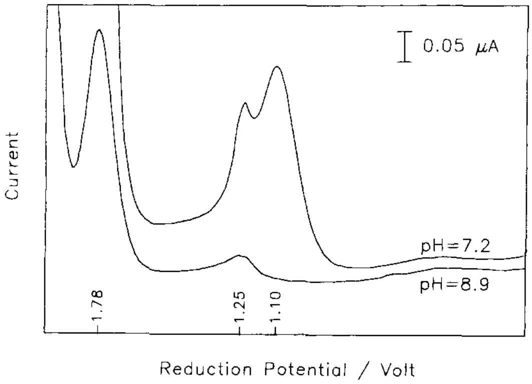


Fig. 5. Differential pulse polarograms of the molybdenum(VI) citrate solution: 1 mM molybdate and 100 mM citrate at $pH_c = 8.9$ and 7.2.

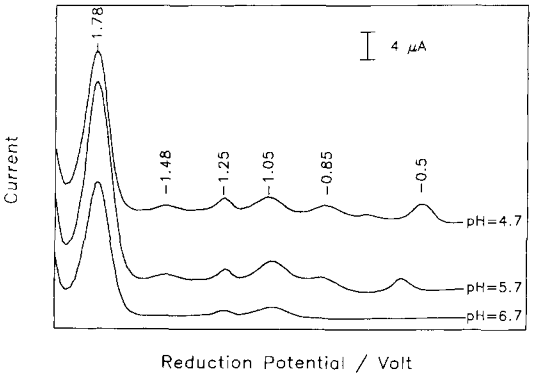


Fig. 7. Differential pulse polarograms of an equimolar solution of molybdate and citrate (0.004 M) at $pH_c = 4.7$, 5.7 and 6.7.

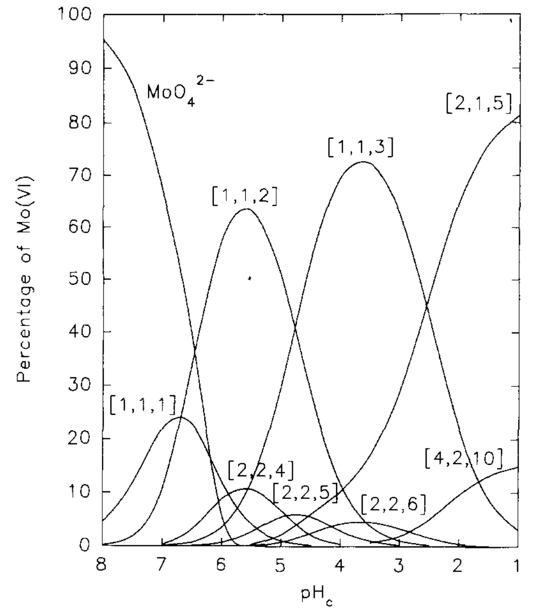


Fig. 8. Distribution of species in the molybdenum(VI) citrate system as a function of pH$_c$ for an equimolar solution (0.004 M).

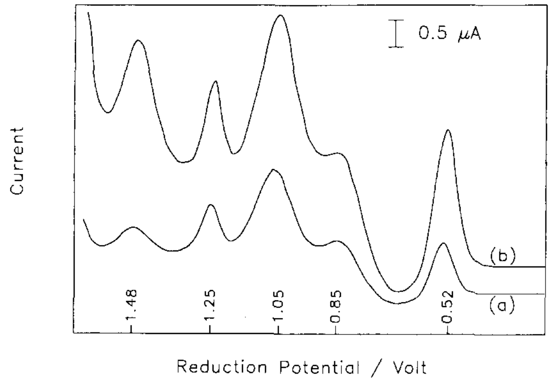


Fig. 9. Differential pulse polarograms of equimolar solutions of molybdate and citrate: (a) 0.004 M and (b) 0.008 M at the same pH$_c$ = 5.7.

about the same. In agreement with this change the height of the peak at −1.48 V increases with the factor *ca* 3.6. For the peak at −0.5 V the factor is only *ca* 2.6, which might indicate that a small amount of some mononuclear complex is also reduced at this potential (or that some other process is taking place simultaneously). In fact, for some solutions containing only mononuclear complexes (polarogram Fig. 5 pH$_c$ = 8.9), a weak peak can be seen at *ca* −0.54 V when the polarogram is run at a much greater sensitivity. Doubling of the total concentrations causes the concentrations of the [1,1,*r*] complexes to increase by a factor of *ca* 1.85 and in accordance with this the peak heights at −1.25, −1.05 and −0.85 increase by factors of 1.83, 1.84 and 1.9, respectively, confirming reduction of the mononuclear complexes at these potentials.

At very low pH, on the other hand, conditions can be chosen for which the [1,2,6]$^{2-}$ complex is the predominant species. For example, at pH$_c$ = 1.4 the percentage concentration of the [1,2,6]$^{2-}$ complex is 98% in a solution with large excess of citrate (1 mM molybdate and 400 mM citrate). From the polarogram shown in Fig. 10 it is seen that new reduction peaks occur at −1.26, −0.64 and −0.31 V. The potentials of these peaks change somewhat when the conditions are changed, for example at pH$_c$ = 3 and higher molybdenum concentration (4 mM molybdate and 40 mM citrate) the reduction peaks occur at −1.22, −0.69 and −0.38 V. An additional strong reduction peak is also observed at −1.6 V, which might be due to the reduction of a [1,2,*r*] complex to a lower valent complex which is stable only under these conditions. In addition to the [1,1,3] complex (*ca* 36%) the solution in question contains only the [1,2,5]$^{3-}$ and [1,2,6]$^{2-}$ complexes (6 and 56%) as major components.

The only other complexes in the system not yet associated with specific reduction peaks are the [2,1,5]$^{2-}$ and [4,2,*r*] complexes. Conditions favourable for the formation of these complexes are relatively low pH$_c$ and some excess of molybdate, but not so much that free molybdenum species would be comparable to the concentration of the complexes in question. By comparing polarograms of an equimolar solution of molybdate and citrate (4 mM) and a solution with molybdate in excess (4 mM molybdate and 2 mM citrate) at two suitable pH$_c$ values, namely 3.0 and 3.7, two new reduction peaks are observed for the solutions containing an excess of molybdate. From the polarograms in Fig. 11 it is seen that the reduction peaks occur at −1.4 and −0.66 V. The former peak can be ascribed to the reduction of the [4,2,10]$^{4-}$ complex, of which the concentration in the two solutions is 0.4 and 12.7%, respectively. The latter peak is not so well defined, but it is most likely due to the reduction of

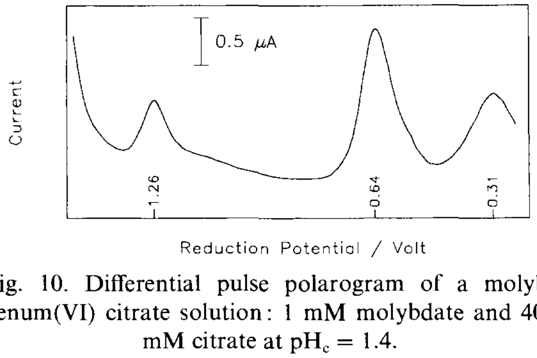


Fig. 10. Differential pulse polarogram of a molybdenum(VI) citrate solution: 1 mM molybdate and 400 mM citrate at pH$_c$ = 1.4.

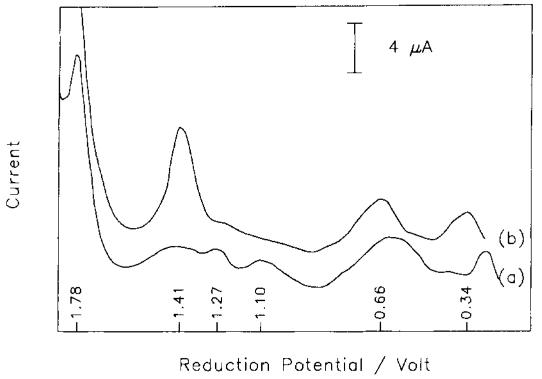


Fig. 11. Differential pulse polarograms at $pH_c = 3.0$: (a) equimolar solution of molybdate and citrate (4 mM) ; (b) a solution with molybdate in excess (4 mM molybdate and 2 mM citrate).

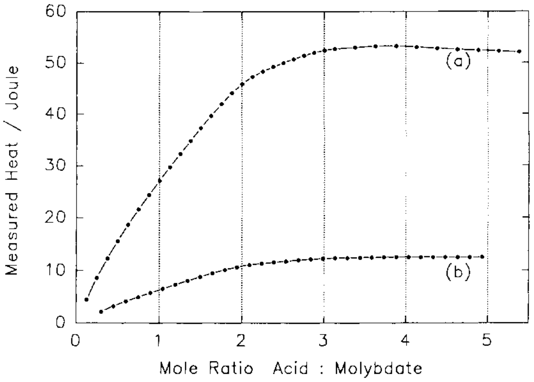


Fig. 12. Measured heat as a function of the molar ratio of acid to molybdate for the titration of equimolar solutions of molybdate and citrate with 1.0 M HCl : (a) 0.04 and (b) 0.01 M.

the $[2,1,5]^{2-}$ complex because it is exhibited by both solutions and stronger in the solution with the highest concentration, but not in direct proportion to the percentage concentrations (29 and 82%). However, the growth of this peak correlates well with the increase in concentration of the $[2,1,5]^{2-}$ complex with pH_c in the range 4.6–2.5 for equimolar solution of molybdate and citrate (4 mM).

Differential pulse polarograms of various other solutions have been recorded to check the agreement between a particular complex and the associated reduction peak. Although due to great overlap of equilibria, peaks are not necessarily well defined or clearly separated under prevailing conditions, their presence in the polarograms always corresponded with the occurrence of the particular complexes in the solutions investigated.

Enthalpimetric investigation

Results obtained in two of the enthalpimetric titrations of equimolar solutions of molybdate and citrate (0.01 and 0.04 M) with hydrochloric acid are shown in Fig. 12, where the total amount of heat measured, Q, is plotted against the molar ratio of acid added to molybdate (or citrate). Extrapolation of the straight-line parts of the curve pertaining to 0.04 mol dm^{-3} indicates discontinuities at mole ratios of acid to molybdate of 2 and 3, in agreement with the formation of major amounts of complexes having 1 : 1 : 2 and 1 : 1 : 3 stoichiometries.

The enthalpy changes for the formation of the complexes were calculated from the measured heat, Q (corrected for dilution effects), by using eq. (4) :

$$Q = \Sigma n_{pqr} \Delta H^0_{pqr}, \tag{4}$$

where n_{pqr} is the number of moles formed and ΔH^0_{pqr} the molar enthalpy change of a given species $[p, q, r]$ at 25°C in NaCl (1.0 M) medium. The set of linear equations obtained from corresponding Q and n_{pqr} values were solved for the unknown ΔH^0_{pqr} parameters using a BMDP least-squares program.[31]

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 eqs (5)–(7) :

$$B = b + \Sigma p \beta_{pqr} b^p c^q h^r \tag{5}$$

$$C = c + \Sigma q \beta_{pqr} b^p c^q h^r \tag{6}$$

$$H = h + \Sigma r \beta_{pqr} b^p c^q h^r, \tag{7}$$

where b, c and h are the equilibrium concentrations of $[MoO_4]^{2-}$, $Hcit^{3-}$ and H^+, respectively.

To account for the rather small amount of heat involved in the protonation of free citrate, previously determined ΔH^0 values were used as fixed parameters in the treatment of the data.[1]

Evaluation of reliable ΔH^0 values for all the species in the pH_c region <2.5 and especially for the minor species is problematical, considering the great overlap of the equilibria. However, from our previous work it is known that ΔH^0 values for the protonation of complex species are rather small so that the quite reasonable approximation, based on the assumption of similar ΔH^0 values for a complex and its protonated form, was introduced. By applying this constraint only where very minor species were involved ($<10\%$) the calculations could be simplified considerably. Further, by equating ΔH^0

values of these species in turn in successive computer runs very reasonable enthalpy changes for all minor species could be obtained, except for the $[1,2,4]^{4-}$, $[1,2,5]^{3-}$ and $[2,1,3]^{4-}$ complexes of which the percentage concentrations were so small under the experimental conditions that it was more meaningful to neglect them altogether.

In order to compensate to some extent for the inherent subjectivity of this strategy and also to check for consistency the different sets of data were treated separately. For the titration pertaining to the lowest concentration (0.01 M), however, only three complexes occur as major components and most of the ΔH^0 parameters for the other complexes had to be fixed in a particular run. Most of the calculations were done with the titration data at the highest concentration, i.e. 0.05 M.

The ΔH^0 values for the various species are listed in Table 1. The error limits are based on the variations observed in the various computations described above, which are more realistic than the narrower limits supplied by the program in a particular run. It is seen that the agreement between these values and those deduced from the change in stability constants with temperature is quite good, considering the respective shortcomings of the methods. In view of this agreement the ΔH^0 values for the minor complexes $[1,2,4]^{4-}$, $[1,2,5]^{3-}$ and $[2,1,3]^{4-}$ obtained from the stability constants at 2 and 25°C can be accepted as reasonable approximations of the true values; these ΔH^0 values could not be calculated from the calorimetric data.

It is meaningful to compare the thermodynamic quantities of the series of mononuclear complexes $[1,1,1]^{4-}$, $[1,1,2]^{3-}$, $[1,1,3]^{2-}$ and $[1,1,4]^{-}$ of molybdenum and tungsten. Both enthalpy and entropy changes show the same pattern. The entropy values for the two systems are very similar whereas the enthalpy values are more favourable for the tungsten complexes by an almost constant amount (12–14 kJ mol^{-1}). The enthalpy change is therefore the cause of the greater stability of the tungsten complexes (*ca* 2 log units in the stability constant). As noted before this result reflects the greater tendency of tungsten(VI) to expand its coordination number from four to six.[3] In polyanion formation the difference in ΔH^0 is *ca* 11–14 kJ mol^{-1} for the change from tetrahedral to octahedral coordination.[4,27] Also noteworthy is the comparable trend in the $T\Delta S^0$ values with successive protonation for the $[1,1,r]$ complexes and citrate itself.

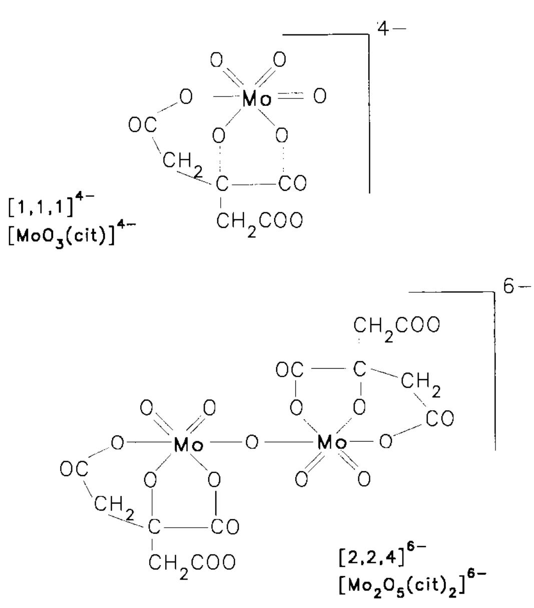
It can be assumed that the structure of the $[2,2,4]^{6-}$ complex of molybdenum is similar to that of tungsten, in which the coordination of citrate is tridentate (Fig. 13). Although the conditions were not stated it has been reported that ^{13}C NMR measurements of a molybdate–citric acid solution indicate that only one of the β-carboxylate groups is not coordinated to molybdenum.[13] It is therefore reasonable to expect tridentate coordination of citrate also in the case of the mononuclear $[1,1,r]$ complexes. Tridentate coordination would have the effect of stabilizing these complexes relative to $[1,2,r]$ complexes, which concurs with the results of this investigation. In equimolar solutions of molybdate and citrate the concentrations of the $[1,2,4]^{4-}$ and $[1,2,5]^{3-}$ complexes are negligible and only the $[1,2,6]$ complex which occurs at low pH$_c$ reaches a concentration of *ca* 10%. In the case of some other α-hydroxycarboxylate ligands, such as lactate and tartrate which coordinate bidentately to molybdenum, some of the $[1,2,r]$ complexes are major species, but in the case of nta (nitrilotriacetate), which coordinates tridentately $[1,2,r]$ complexes do not occur.[2,3,5,24]

It is interesting to compare the thermodynamic quantities for the following reactions:

$$\mathrm{MoO_4^{2-} + Hcit^{3-} + 2H^+ \rightleftharpoons [MoO_3(Hcit)]^{3-}} \quad (8)$$

$$\mathrm{MoO_4^{2-} + nta^{3-} + 2H^+ \rightleftharpoons [MoO_3(nta)]^{3+}} \quad (9)$$

The entropy change is very similar ($T\Delta S^0 = 32$ and 30 kJ mol^{-1}) as one would expect from the tridentate behaviour of the two ligands.[2] The enthalpy change for the citrate complex, however, is not as favourable as that for the nta complex ($\Delta H^0_{112} = -55.6$ and -69.1 kJ mol^{-1}). This


$[1,1,1]^{4-}$
$[\mathrm{MoO_3(cit)}]^{4-}$

$[2,2,4]^{6-}$
$[\mathrm{Mo_2O_5(cit)_2}]^{6-}$

Fig. 13. Proposed structures of the mononuclear and dinuclear complexes of molybdenum(VI) and citrate.

difference can be explained in terms of the energy cost to deprotonate the α-hydroxy group of citrate (p$K = 11.6^{32}$), which acts as a donor together with the central carboxylate group in forming a stable five-membered ring; the energy cost is only partly recovered in the protonation of the uncoordinated carboxylate group. The $[1,1,2]^{3-}$ and $[2,2,4]^{6-}$ complexes occur in the same pH$_c$ region. The equilibrium constant for the dimerization reaction (10):

$$2[MoO_3(citH)]^{2-} \rightleftharpoons [Mo_2O_5(cit)_2]^{6-} + H_2O, \quad (10)$$

is rather small, log $K = 1.02$, and it is only at relatively high concentration (0.1 M) that the monomer and dimer would occur in equal amounts at 25°C. The thermodynamic parameters ($\Delta H^0 = -28.6$ and $T\Delta S^0 = -22.7$ kJ mol^{-1}) show that the reaction is enthalpy driven opposed by an unfavourable entropy change.

CONCLUSION

By varying the pH$_c$ and concentrations of the reactants over a wide range, complexes with six different ratios of molybdenum : citrate have been identified, namely 1 : 1, 1 : 2, 2 : 2, 2 : 1, 4 : 2 and 4 : 4; the existence of the latter complex is uncertain. The variety in stoichiometry is a direct consequence of the coordination characteristics of citrate and the typical behaviour of molybdate towards α-hydroxycarboxylate ligands. The complexes can be described as follows: the mononuclear complexes $[MoO_3(cit)]^{4-}$ and $[MoO_3(Hcit)_2]^{6-}$ and their protonated forms, the dinuclear complexes $[Mo_2O_5(cit)_2]^{6-}$ and $[Mo_2O_5(cit)(H_2O)_3]^{4-}$ and their protonated forms, and finally the tetranuclear complex $[Mo_4O_{11}(cit)(Hcit)]^{5-}$ and its protonated form $[Mo_4O_{11}(Hcit)_2]^{4-}$. The formulae used are based on the structures shown in Fig. 13; tridentate coordination of citrate with molybdenum(VI) can be assumed on the grounds of known structures of the two compounds $[(CH_3)_3N(CH_2)_6N(CH_3)_3]_2[MoO_4O_{11}(Hcit)_2] \cdot 12H_2O$[14] and $Na_6[W_2O_5(cit)_2] \cdot 10H_2O$.[12]

Thermodynamic quantities for the major complexes have been determined. Enthalpy changes determined by calorimetry agree satisfactorily with those calculated from formation constants determined at 25 and 2°C. Differential pulse polarography has been applied quite successfully to verify the existence of a number of complexes.

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