Molybdenum(VI) Complex Formation. Part 4.† Equilibria and Thermodynamic Quantities for the Reactions with Tartrate in 1.0 mol dm^{-3} Sodium Chloride

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Complex formation between molybdate and tartrate has been investigated in the pH$_c$ range 1.2—7.5 by potentiometric and enthalpimetric titrations at 25 °C in 1.0 mol dm^{-3} sodium chloride. The potentiometric data were treated with the computer program SUPERQUAD taking into account all side reactions of molybdate and tartrate with hydrogen ions. The 'best' reaction model comprises ten complexes, representing four different molybdate–tartrate stoicheiometries. The formation constants of the complexes, denoted by β_{pqr}, where the subscripts p, q, and r refer to the stoicheiometric coefficients in the general formula $[(MoO_4)_p(C_4H_4O_6)_qH_r]^{(2p+2q-r)-}$, have the values: log β_{122} = 16.33, log β_{123} = 19.99, log β_{124} = 22.92, log β_{214} = 24.81, log β_{215} = 26.16, log β_{447} = 56.22, log β_{448} = 61.53, log β_{449} = 63.98, log β_{426} = 43.4, and log β_{427} = 48.2. Enthalpy and entropy changes for all the complexes, except $(4,2,6)^{6-}$ and $(4,2,7)^{5-}$ which are minor species, were evaluated from the enthalpimetric data using the values of these formation constants. Equilibrium constants as well as enthalpy and entropy changes for the protonation of tartrate in 1.0 mol dm^{-3} NaCl have also been determined, log β_{011} = 3.69 and log β_{012} = 6.38.

Complex formation between molybdenum(VI) and tartrate has been demonstrated by several authors using a variety of techniques, *e.g.* potentiometry, conductometry, polarimetry, circular dichroism, and n.m.r. spectroscopy.[1–9] Evidence for the existence of complexes with a molybdate to tartrate ratio of 1:1[3,9] and 1:2[1,2,8,9] have been reported. A polynuclear complex with 1:1 molybdate to tartrate ratio has been proposed by Cadiot *et al.*[4] while evidence for the formation of polynuclear complexes was also obtained by other workers.[3,6,7] Recently n.m.r. work indicated the existence of four major complexes and also provided useful structural information about some of these complexes, *i.e.* complexes having a molybdate:tartrate ratio of 1:1 and 1:2 are bonded *via* a carboxylic oxygen atom and the adjacent hydroxyl oxygen atom.[9] The other two main species contain bridging tartrate and are assumed to be polynuclear but their 'nature is not as clear as that of the complexes containing only terminally co-ordinated ligands.'[9] The authors suggested a 2:2 species analogous to a dinuclear complex which they isolated in the solid state. The nature of the other polynuclear complex has yet to be determined.

From the previous work summarized above it may be concluded that 1:1 and 1:2 complexes as well as polynuclear complexes, of which the composition is still uncertain, occur in solution. However, the exact stoicheiometry in terms of all three reactants (MoO_4^{2-}: tartrate: H^+) of none of these complexes is known. Also lacking is information about the equilibria and formation constants for the various possible complexes. Not only is such information vital for a complete elucidation of this complicated system, but it is also essential for the interpretation of data obtained by several other experimental methods *inter alia* calorimetry.

In this paper we report the results of a potentiometric and calorimetric investigation of molybdenum(VI)–tartrate complex formation. Equilibrium analysis of the potentiometric data using the computer program SUPERQUAD[10] led to the identification of mononuclear, dinuclear, and tetranuclear complexes occurring in different states of protonation. Using the now known equilibrium constants the enthalpy and entropy changes for the formation of the various complexes were calculated from the calorimetric data.

Experimental

Reagents and Solutions.—All reagents were of analytical grade and solutions were prepared with water obtained from a Millipore Milli-Q system. Sodium molybdate and sodium chloride solutions were prepared from the recrystallized salts (Merck) and standardized gravimetrically as described previously.[11] L-(+)-Tartaric acid (Riedel–De Haën) was recrystallized and dried in a vacuum oven. Hydrochloric acid was standardized indirectly against potassium hydrogenphthalate by titration with sodium hydroxide.

Potentiometric Titrations.—Titrations were carried out at 25 °C using a Metrohm 636 Titroprocessor, fitted with a 20-cm^3 burette. Typically 80 or 90 cm^3 of a mixture of molybdate and tartaric acid (or the neutralized acid) were titrated with sodium hydroxide (or hydrochloric acid); forward and reverse titrations produced similar F *vs.* pH$_c$ curves (Figure 1). The initial concentrations (mol dm^{-3}) of molybdate and tartrate, respectively, were as follows: 0.05, 0.01; 0.05, 0.025; 0.05, 0.05; 0.01, 0.01; 0.025, 0.05; and 0.01, 0.05. The pH$_c$ range covered was 7.5—2.0 except for the titration of the 0.05, 0.05; and 0.05, 0.025 mol dm^{-3} molybdate–tartrate solutions for which the measurements were extended to pH$_c$ ≈ 1.2. This was necessary to create conditions which were favourable for the formation of the $(2,1,4)^{2-}$ and $(2,1,5)^{-}$ complexes (*cf.* Discussion for explanation). Titrations were carried out in duplicate and checked for consistency by comparing the residuals diagrams produced by SUPERQUAD.[10] Some of these titrations were done manually to ensure that possible slow reactions were not overlooked. Stable potentials were obtained within seconds after addition of the titrant. In the final computer analyses some of the duplicate titrations were left out in order to limit the data to 600 points. All solutions were made 1.0 mol dm^{-3} with respect to chloride ions by addition of sodium chloride. A stream of purified nitrogen was passed through 1.0 mol dm^{-3} NaCl and then bubbled slowly through the titration solution. The free hydrogen concentration, h, was determined by measuring the potential, E, to ±0.2 mV using a Ross combination electrode (Orion) with a 3 mol dm^{-3} KCl bridge solution. Equation (1)

$$E = E^0 + 59.16 \log h + E_j \qquad (1)$$

was used to calculate h from the measured potential at each

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† Part 3 is ref. 24.

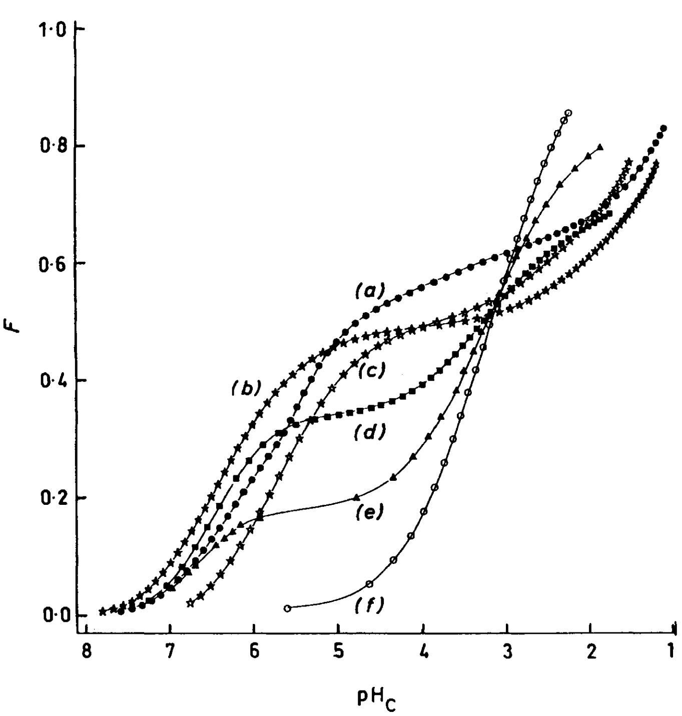

Figure 1. Function *F versus* pH_c for some representative potentiometric titrations. Initial concentrations, molybdate:tartrate: (*a*) 0.05:0.025; (*b*) 0.05:0.05; (*c*)0.01:0.01; (*d*) 0.025:0.05; (*e*) 0.01:0.05; (*f*) 0:0.02 mol dm^{-3}

titration point. Values for E^0 and E_j were determined from titrations of 1.0 mol dm^{-3} NaCl with hydrochloric acid as described by Rossotti.[12] For brevity $-\log h$ is denoted by pH_c.

Enthalpimetric Titrations.—An isothermal titration calorimeter, Tronac model 550, described elsewhere,[13,14] was used to measure the enthalpy of complex formation. Solutions containing molybdate and tartrate (20 cm^3) were titrated with hydrochloric acid from a Gilmont precision microburette (2.5 cm^3) and the data collected as described previously.[11] Again, all solutions were made 1.0 mol dm^{-3} with respect to chloride by addition of sodium chloride. The initial concentrations of molybdate and tartrate respectively were 0.05, 0.05; 0.025, 0.05; and 0.025, 0.10 mol dm^{-3}. These titrations were carried out in duplicate and the pH_c range covered was 7.5—1.2. A blank titration was done to correct for the heat of dilution (endothermic) which varied from ≈0.40 to 0.32 kJ mol^{-1} of hydrochloric acid added and amounted to ≈1—2% (depending on the titration conditions) of the total heat measured. The heat of reaction for the protonation of tartrate was determined in separate titrations of 0.1 mol dm^{-3} sodium tartrate (1.0 mol dm^{-3} Cl^-) with 1.0 mol dm^{-3} hydrochloric acid. For these titrations the correction for the endothermic dilution effect amounted to ≈15% of the reaction enthalpy measured.

Results and Discussion

Potentiometric Investigation.—The equilibria for all the possible protonation, condensation, and complexation reactions of molybdate and tartrate are represented by the general equation (2). For brevity species will often be described in terms of the stoicheiometric coefficients which define their composition, *i.e.* $(p,q,r)^{(2p+2q-r)-}$. Formation constants are denoted by β_{pqr}.

$$p[MoO_4]^{2-} + qC_4H_4O_6^{2-} + rH^+ \rightleftharpoons [(MoO_4)_p(C_4H_4O_6)_qH_r]^{(2p+2q-r)-} \quad (2)$$

The results of some representative titrations of tartrate and of mixtures of tartrate and molybdate with hydrochloric acid are represented as normalized curves in Figure 1 where *F* is plotted against pH_c. The function, *F*, which represents the fraction of the total negative charge of molybdate and tartrate neutralized due to protonation, is given by equation (3), where *H*, *B*, and *C*

$$F = \frac{H - h}{2(B + C)} \quad (3)$$

are the total analytical concentrations of hydrochloric acid, molybdate, and tartrate respectively. It is known from previous work that several complexes occur in this system. For the titrations of equimolar solutions of molybdate and tartrate an inflection is shown by the *F vs.* pH_c curves at $F \approx 0.5$ indicating the formation of a rather stable complex at $pH_c \approx 4$, corresponding to a (*p,q,r*) stoicheiometry of (1,1,2). The effect of concentration on the shape of these two curves (0.01 and 0.05 mol dm^{-3}) suggests that a polynuclear complex is involved. The inflections exhibited by the curves for which tartrate is in excess show that, after all molybdenum has reacted, little protonation takes place until the pH_c is low enough for free tartrate to become protonated and *F* then begins to increase again. From the curves in Figure 1 it is also seen that at low pH_c protonation of the complexes is more difficult than that of tartrate, contrary to the situation at high pH_c.

For titrations with excess of either molybdate or tartrate provision must be made in the computer treatment of the data for side equilibria involving uncomplexed molybdate or tartrate. The molybdenum(VI) species, $[HMoO_4]^-$, $[MoO_3(H_2O)_3]$, $[MoO_2(OH)(H_2O)_3]^+$, $[HMo_2O_7]^-$, $[Mo_7O_{24}]^{6-}$, $[HMo_7O_{24}]^{5-}$, $[H_2Mo_7O_{24}]^{4-}$, $[H_3Mo_7O_{24}]^{3-}$, $[Mo_8O_{26}]^{4-}$, and $[HMo_2O_6]^+$ were taken into account using previously determined equilibrium constants pertaining to 1.0 mol dm^{-3} NaCl medium at 25 °C.[15–17] Inclusion of the latter species was necessary only for data at $pH_c < 2$ where its maximum percentage concentration (in terms of total Mo) reached 7%.

Equilibrium constants for the protonation of tartrate in 1.0 mol dm^{-3} NaCl were calculated from data obtained in separate potentiometric titrations. The values obtained, $\log \beta_{011} = 3.69 \pm 0.01$ and $\log \beta_{012} = 6.38 \pm 0.01$ (error limits 3σ), can be compared with those reported[18] for 1.0 mol dm^{-3} $NaClO_4$ namely $\log \beta_{011} = 3.72$ and $\log \beta_{012} = 6.48$.

The titration data were treated with the computer program SUPERQUAD[10] to search for a reaction model that would give the best description of the data. Species taken into account in the calculations are automatically rejected if their formation constants are ill defined (standard deviation >33% of the value). The features of this powerful program have been described previously.[10] Numerous reaction models were considered comprising various combinations of possible complexes with *p* and *q* values of up to four; for each possible complex a number of reasonable *r* values was considered. A few complexes with $p = q = 5$ and 6 were tested but did not improve the final model.

The model testing was first limited to data pertaining to $pH_c > 2.0$ and later extended to still lower pH_c to confirm the presence of those complexes occurring in relatively small concentrations at $pH_c < 2.0$. Although calculations had been based on different initial models which were improved by either rejection (by the program) or addition of various possible species, the best model (smallest sample standard deviation, *s*)[10] could always be obtained irrespective of the strategy followed. This model comprised ten complexes, representing four

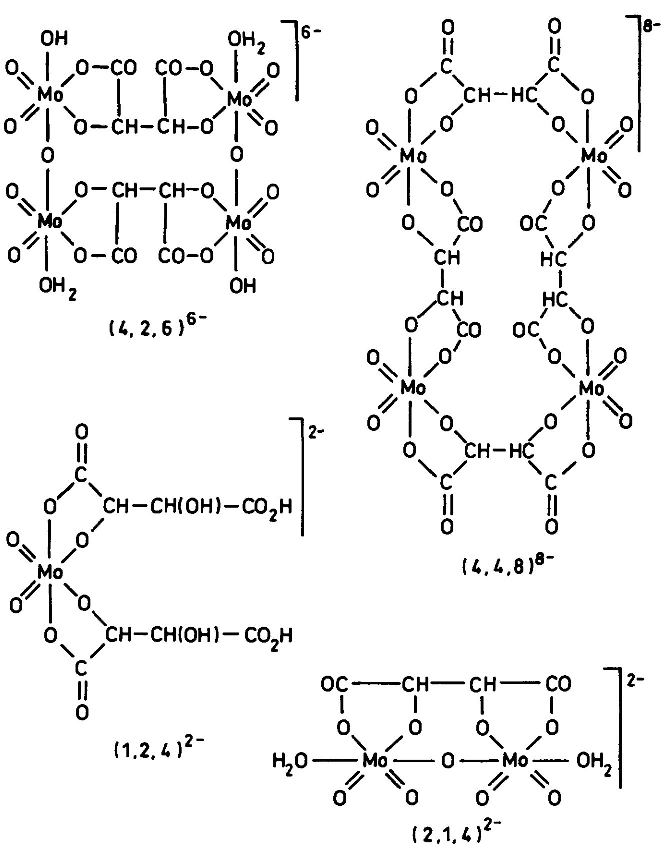

Figure 2. Proposed structures for the complexes of Mo^{VI} with tartrate

different molybdenum–tartrate stoicheiometries, *i.e.* the monomeric complexes $(1,2,2)^{4-}$, $(1,2,3)^{3-}$, $(1,2,4)^{2-}$, the dimeric complexes $(2,1,4)^{2-}$, $(2,1,5)^{-}$, and two types of tetrameric complexes: $(4,4,7)^{9-}$, $(4,4,8)^{8-}$, $(4,4,9)^{7-}$, and $(4,2,6)^{6-}$, $(4,2,7)^{5-}$. The value of $s = 4.28$, based on estimated errors of 0.01 cm^3 in the volume and 0.002 in the pH_c for a total of 11 titrations, extending over a very wide pH_c range, signifies a particularly good fit (Table, run A). The relative standard error was greater than 4% for only three of the complexes namely, 7, 28, and 13% for the $(4,4,9)^{7-}$, $(4,2,6)^{6-}$, and $(4,2,7)^{5-}$ species respectively. The last two complexes are present in relatively low percentages, the maximum (in terms of Mo) under the present experimental conditions being 7 and 20% respectively; for the other complexes the maximum is >40%. The $(4,2,6)^{6-}$ species must therefore be regarded as a minor complex the existence of which could be questioned.

Another computer run was therefore carried out omitting the titration data pertaining to a five-fold excess of molybdate over tartrate. These data points contributed the least to the characterization of the system while introducing the greatest uncertainties because of the presence of relative large percentages of uncomplexed molybdate species. The reaction model was retained, however, and the fit improved while insignificant changes in the log values of the formation constants occurred (Table, run B). The possibility that a wrong model has been arrived at because of possible errors introduced by the equilibrium constants of the side equilibria can therefore be ruled out. Also, two additional runs with all the data showed that refinement of either the tartrate protonation constants or the formation constants of $[Mo_7O_{24}]^{6-}$ and $[HMo_7O_{24}]^{5-}$, together with those of the complexes, yielded consistent results. None of the complexes was rejected and the values of their formation constants were practically identical to those obtained in the previous runs. Furthermore, the values of the tartrate protonation constants as well as the formation constants of $[Mo_7O_{24}]^{6-}$ and $[HMo_7O_{24}]^{5-}$ agreed very well with those determined independently in previous investigations (Table, runs C and D).

Having ruled out possible inconsistencies in the system one can only question the model in terms of an accidental combination of species that may have resulted in the good fit. One possible way of checking for such a coincidence is to treat the data differently, for example by minimizing some other function instead of the measured potential as is done by means of SUPERQUAD. Such a check was in fact carried out by minimizing the function F defined by equation (3). Expressed in terms of the formation constants and equilibrium concentrations of the various species F is given by equation (4).

$$F = \frac{\Sigma r b^p c^q h^r \beta_{pqr}}{2(b + \Sigma p b^p c^q h^r \beta_{pqr} + c + \Sigma q b^p c^q h^r \beta_{pqr})} \qquad (4)$$

A non-linear least-squares program BMDPAR[19] was adapted to fit the $F(pH_c)$ data by calculating values for the equilibrium constants. A subroutine was written to calculate the free molybdenum and tartrate concentrations by iteration from the total concentrations and pH_c at each experimental point using equations (5) and (6).

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

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

The values obtained for the formation constants are given in the Table. It is seen that these values are practically identical to those obtained by means of SUPERQUAD, while the theoretical curves fitted very well with the experimental points (Figure 1). Consequently, from a mathematical point of view there seems to be no reason to doubt the validity of the proposed reaction model.

In the light of previous work on complex formation of molybdenum(VI) with α-hydroxy carboxylic acids, and tartaric acid in particular, all the species included in the model are quite acceptable. Evidence obtained for complexes with a Mo:tartrate ratio of 1:2 is in agreement with the $(1,2,2)^{4-}$, $(1,2,3)^{3-}$, and $(1,2,4)^{2-}$ complexes now characterized. Sodium salts of these complex ions have also been prepared by Gil and co-workers[9] for example $Na_2[MoO_2\{(+)\text{-}C_4H_4O_6\}_2]\cdot 4(CH_3)_2SO$. The 1:2:*r* stoicheiometry seems to be favoured in the case of α-hydroxy carboxylic acids[8,9,20,21] in contrast to the 1:1:*r* stoicheiometry which dominates in the case of oxalic acid.[11] Possible structures for the complexes are given in Figure 2.

The polynuclear complex of unknown composition previously postulated by different authors[4,6,7,9] has now been identified as tetranuclear and exists in three different states of protonation, of which $(4,4,8)^{8-}$ is the predominant form (Figures 3 and 4). The ring structure proposed for this complex, shown in Figure 2, is based on thermodynamic evidence and is discussed in the next section. Its ionized form, $(4,4,7)^{9-}$, is assumed to have a chain structure.

The other two tetrameric complexes $(4,2,6)^{6-}$ and $(4,2,7)^{5-}$ occur in significant concentrations only in solutions where molybdate is in excess. The identification of the latter complex is of special interest in view of the $(4,2,8)^{4-}$ malate[22,23] and $(4,2,10)^{4-}$ citrate[24] complexes isolated and structurally characterized by single-crystal *X*-ray analyses. The stoicheiometry of the $(2,1,4)^{2-}$ and $(2,1,5)^{-}$ complexes agree with that reported for complexes identified in the molybdenum–citrate system.[25] The results of the present investigation do not support some

Table. Results of various reaction models with SUPERQUAD[10] (runs A—D) and with BMDP[19] (run E)

	Reaction models (log β_{pqr})							
Complex	A	B[a]	C	D	E	$\Delta G^{0\,b}$	$\Delta H^{0\,b}$	$T\Delta S^{0\,b}$
$(1,2,2)^{4-}$	16.33	16.33 ± 0.02	16.33	16.33	16.32	−93.2	−81	12
$(1,2,3)^{3-}$	19.99	19.99 ± 0.03	19.99	19.99	20.00	−114.1	−87	28
$(1,2,4)^{2-}$	22.92	22.92 ± 0.03	22.90	29.93	22.92	−130.9	−85	46
$(2,1,4)^{2-}$	24.81	24.81 ± 0.03	24.80	24.80	24.66	−141.7	−116	25
$(2,1,5)^{-}$	26.18	26.16 ± 0.04	26.14	26.19	26.20	−149.3	−117	32
$(4,4,7)^{9-}$	56.23	56.22 ± 0.05	56.23	56.21	56.21	−320.9	−290	31
$(4,4,8)^{8-}$	61.53	61.53 ± 0.05	61.52	61.53	61.37	−351.3	−349	2
$(4,4,9)^{7-}$	63.99	63.98 ± 0.08	63.99	63.99	64.09	−365.3	−327	39
$(4,2,6)^{6-}$	43.33	43.41 ± 0.33	43.35	43.57	43.48			
$(4,2,7)^{5-}$	48.13	48.17 ± 0.15	48.13	48.21	48.33			
$(0,1,1)^{-}$	*c*	*c*	3.70	*c*	*c*	−21.19	−3.1	18
$(0,1,2)$	*c*	*c*	6.41	*c*	*c*	−36.4	−7.0	29
$(7,0,8)^{6-}$	*c*	*c*	*c*	52.74	*c*			
$(7,0,9)^{5-}$	*c*	*c*	*c*	57.06	*c*			
s[d]	4.28	3.92	4.2	4.1	$\sigma_F = 0.0054$			
χ^2	14	15	11	17				

[a] Error limits ±3σ. [b] kJ mol^{-1}. [c] Constants fixed at values obtained in independent experiments: log β_{011} = 3.69, log β_{012} = 6.38, log β_{708} = 52.87, and log β_{709} = 57.39. [d] Sample standard deviation.

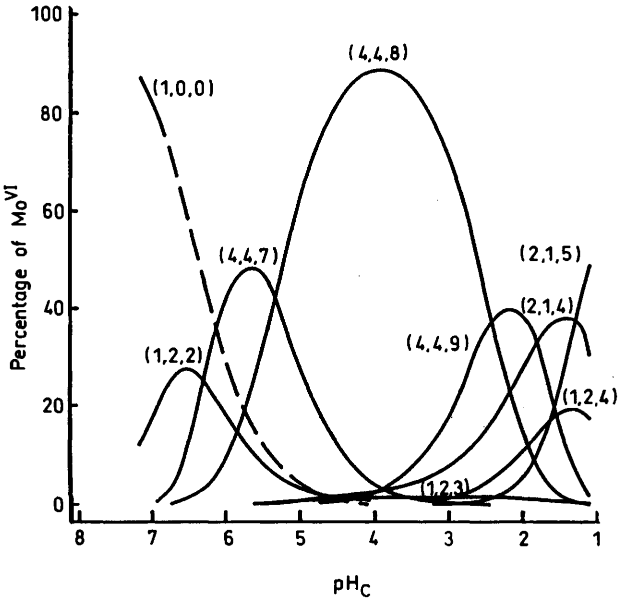

Figure 3. Variation of concentration of complexes, expressed as a percentage of the total molybdenum(VI) concentration, as a function of pH$_c$ during a titration of an equimolar solution of molybdate and tartrate (0.05 mol dm^{-3}) with hydrochloric acid

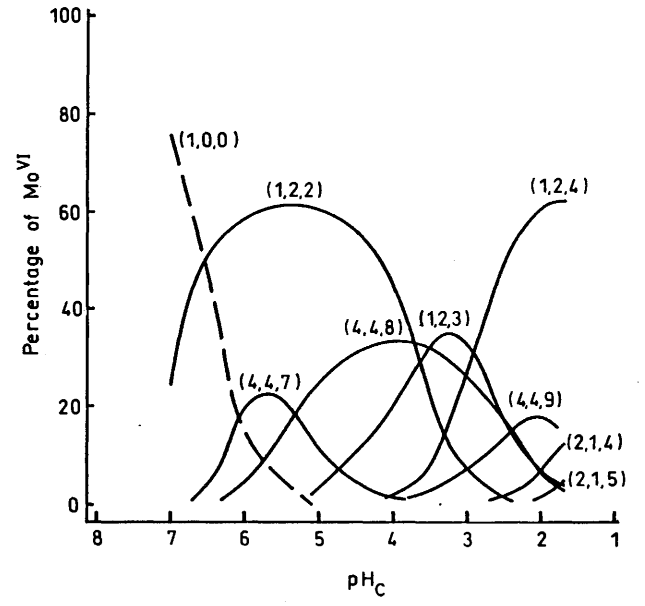

Figure 4. Variation of concentration of complexes, expressed as a percentage of the total molybdenum(VI) concentration, as a function of pH$_c$ during a titration of a solution of 0.025 mol dm^{-3} molybdate and 0.05 mol dm^{-3} tartrate with hydrochloric acid

previous claims of predominant monomeric and dimeric complexes with a Mo:tartrate ratio of 1:1.

In our opinion the reaction model for this system had been established with sufficient certainty to justify a calorimetric investigation; the results of such an investigation are described in the next section.

Calorimetric Investigation.—Conditions chosen for the enthalpimetric titrations were such that relatively high concentrations of all the complexes except $(4,2,6)^{6-}$ and $(4,2,7)^{5-}$ could be obtained. The concentrations of the latter species are negligible unless an excess of molybdate is added. Any excess of molybdate had to be avoided because ΔH^0 values (25 °C, 1.0 mol dm^{-3} NaCl) needed to correct for the heat involved in the protonation and condensation reactions of free molybdate are not available.

The results of two enthalpimetric titrations are shown in Figure 5 where the total amount of heat measured, Q, is plotted against the molar ratio of acid added to molybdate. A break in each of the curves occurs at a mole ratio of 2:1 which indicates that the formation of a predominant complex with $(1,q,2)$ stoicheiometry has been completed at that point. This finding is consistent with the distribution of species shown in Figures 3 and 4. The $(1,2,2)^{4-}$ and $(4,4,8)^{8-}$ complexes reach their maximum percentages at pH$_c$ values which coincide with the mole ratio indicated by the enthalpy curves. The presence of excess of tartrate has little effect on the position of the break because very little protonation of free tartrate takes place at pH$_c$ < 5 (Figure 1).

The enthalpy changes for complex formation were calculated from the measured heat (corrected for dilution effects) using

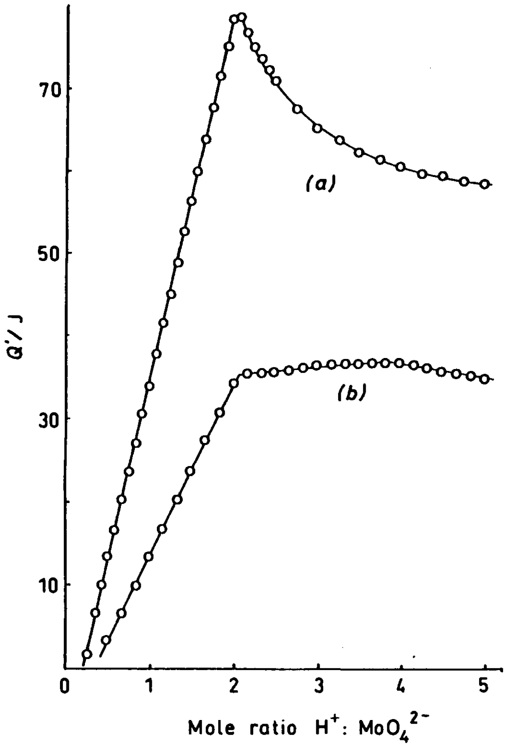

Figure 5. Measured heat, Q', has a function of the molar ratio of acid to molybdate for a titration of (*a*) an equimolar solution of molybdate and tartrate (0.05 mol dm^{-3}) and (*b*) a solution of 0.025 mol dm^{-3} molybdate and 0.05 mol dm^{-3} tartrate, both with 1 mol dm^{-3} HCl (Q' = total heat minus heat generated during first two increments of acid added)

equation (7), where n_{pqr} is the number of moles formed and

$$Q = \Sigma n_{pqr}\Delta H^0_{pqr} \qquad (7)$$

ΔH_{pqr} is the molar enthalpy change for the formation of a given species at 25 °C in 1.0 mol dm^{-3} NaCl medium. Values for n_{pqr} at each titration point were calculated from the concentrations of the species obtained by simultaneous solution of the three mass-balance equations (5), (6), and (8).

$$H = h + \Sigma r b^p c^q h^r \qquad (8)$$

This was done in a subroutine supplied to the BMDP least-squares program[19] employed to solve the set of linear equations obtained from the $Q(n_{pqr})$ data. The enthalpy changes involved in the protonation of free tartrate, *i.e.* ΔH^0_{011} and ΔH^0_{012}, had been determined in separate titrations (Table 1) and these values were introduced as fixed parameters in the calculations of the ΔH^0_{pqr} values for complexation.

The enthalpy changes determined for the $(2,1,4)^{2-}$ and $(2,1,5)^{-}$ molybdenum tartrate complexes namely $\Delta H^0_{214} = -116$ and $\Delta H^0_{215} = -117$ kJ mol^{-1} can be compared with those reported for the $(2,1,4)^{3-}$ and $(2,1,5)^{2-}$ complexes of molybdenum with citrate,[25] *i.e.* -124 and -125 kJ mol^{-1} respectively. Thermodynamic quantities for complexes with a Mo:ligand ratio of 1:2 have not been reported previously, but it is informative to relate the enthalpy change for the $(1,2,r)^{(6-r)-}$ molybdenum tartrate complexes (-81, -87, and -85 kJ mol^{-1}) with that of the $(1,1,2)^{2-}$ and $(1,1,2)^{3-}$ complexes of oxalate and citrate (-60.2 and -59.5 kJ mol^{-1} respectively).[11,25] If the enthalpy change for a $(1,1,2)^{2-}$ tartrate complex were comparable to that of the latter oxalate and citrate complexes it would mean that the co-ordination of a second tartrate is favoured by about 20 kJ mol^{-1}. Such a favourable enthalpy change for the conversion of tartrate complexes with a Mo:ligand ratio of 1:1 into those with a ratio of 1:2 might well be the reason why 1:1 complexes do not feature in this system. It is conceivable that measurable concentrations of 1:1 tartrate complexes could occur under special conditions, for example in solution with excess of molybdate, but then only at high dilution when competition with polyions would be limited.

The enthalpy and entropy changes for the successive protonation of the various species are typical of what one would expect for such reactions[11,25,26] except those for the protonation of the $(4,4,7)^{9-}$ complex which can be rationalized in terms of the structures proposed. Protonation of an anionic base normally results in a rather small negative or positive ΔH^0, while $T\Delta S^0$ will have a value of $\approx 25 \pm 10$ kJ mol^{-1} (T = 298 K). The relatively large ΔH^0 value for the protonation of the $(4,4,7)^{9-}$ complex (-59 kJ mol^{-1}) is explained in terms of the change from a chain structure to a ring structure. Protonation would permit co-ordination of the tartrate 'end' of the chain to the molybdate 'end' effecting ring closure and the formation of another five-membered ring. Consistent with this explanation is the fact that a typical $T\Delta S^0$ value for protonation is not obtained because of the decrease in entropy when the chain structure is converted into a ring structure. A decrease in entropy is expected with ring closure due to the decrease in the number of ways that energy can be stored by the complex.

Conclusion

The results of this investigation show that complexes with four different ratios of Mo:tartrate exist in solution: the three monomeric complexes $[MoO_2(HL)_2]^{4-}$, $[MoO_2(HL)(H_2L)]^{3-}$ and $[MoO_2(H_2L)_2]^{2-}$, two dimeric complexes $[Mo_2O_5(OH_2)_2L]^{2-}$ and $[HMo_2O_5(OH_2)_2L]^{-}$, and two types of tetrameric complexes, $[(MoO_2)_4(OH)_2(HL)L_3]^{9-}$, $[(MoO_2L)_4]^{8-}$, $[H(MoO_2L)_4]^{7-}$, and $[\{Mo_2O_5(OH)(OH_2)L\}_2]^{6-}$, $[(Mo_2O_5L)_2(OH)(OH_2)_3]^{5-}$. Formulation of the complexes is based on the structures proposed in Figure 2, with the tartrate anion, $C_4H_4O_6^{2-}$, denoted by H_2L^{2-}. It is assumed, in accordance with n.m.r. evidence,[9] that tartrate co-ordinates with molybdenum by means of a carboxylic oxygen and the adjacent hydroxyl oxygen to form a five-membered ring with molybdenum. Co-ordination of one tartrate to two molybdenum centres is therefore possible and this leads to the formation of dimeric and tetrameric complexes.

Stability constants have been obtained for all the complexes and species distribution curves show that $[MoO_2(HL)_2]^{4-}$ and $[(MoO_2L)_4]^{8-}$ are the two most stable complexes. The thermodynamic quantities ΔH^0 and ΔS^0 for complexation have been calculated from calorimetric data using the now known stability constants. The ΔH^0 and ΔS^0 values obtained for the complexes $[(MoO_2)_4(OH)_2(HL)L_3]^{9-}$ and $[(MoO_2L)_4]^{8-}$ are consistent with a chain and ring structure respectively.

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