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Tungsten(VI) complex formation. Equilibria and thermodynamic quantities for the reactions with malate

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Complex formation between tungstate and malate has been investigated in the range pH 1.5–8.5 by potentiometric and enthalpimetric titrations at 25 °C in 1.0 mol $\mathrm{dm^{-3}}$ (Na)Cl. The 'best' reaction model comprises mono-, di- and tetra-nuclear 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 $[(\mathrm{WO_4})_p(\mathrm{mal})_q\mathrm{H}_r]$, have the values: $\log \beta_{111} = 8.85$, $\log \beta_{112} = 14.78$, $\log \beta_{113} = 17.26$, $\log \beta_{122} = 17.20$, $\log \beta_{123} = 21.70$, $\log \beta_{124} = 25.61$, $\log \beta_{213} = 23.07$, $\log \beta_{222} = 18.87$, $\log \beta_{223} = 25.72$, $\log \beta_{224} = 31.88$ and $\log \beta_{4411} = 73.60$. Enthalpy and entropy changes for complexes occurring in sufficiently high concentrations were calculated from the calorimetric data using these formation constants: $\Delta H^\circ_{111} = -64$, $\Delta H^\circ_{112} = -65$, $\Delta H^\circ_{113} = -67$, $\Delta H^\circ_{122} = -86.0$, $\Delta H^\circ_{123} = -92$, $\Delta H^\circ_{124} = -91$, $\Delta H^\circ_{222} = -115$, $\Delta H^\circ_{223} = -121$, $\Delta H^\circ_{224} = -120$ and $\Delta H^\circ_{4411} = -240$ kJ $\mathrm{mol^{-1}}$.

This investigation is a continuation of our research on the complexation of molybdenum(VI) and tungsten(VI) with different carboxylate and hydroxycarboxylate ligands. The research is directed at the identification and characterization of the various complexes in terms of structure, stability and thermodynamic quantities. Despite the complexity of the systems which is further exacerbated by the tendency of molybdenum(VI) and tungsten(VI) to form polyoxoanions, a reasonably clear picture of the co-ordination behaviour of these elements has emerged from these and other studies reported in the literature. Typically, mono-, di- and tetra-nuclear complexes, protonated to various extents, have been found to exist in solution, some of which are often only minor species. A small number of these complexes have been isolated in the solid state and characterized by X-ray analysis. Previous investigations of the complexation of tungsten(VI) with malate [malic acid, $\mathrm{H_3mal = CH(OH)(CO_2H)CH_2CO_2H}$] have shown the presence of complexes having 1:1, 2:2, 2:1 and 1:2 tungstate:malate stoichiometries.[1,2] Proton NMR spectroscopy has been used by Gil *et al.*[1] to demonstrate the existence of four complexes namely 1:2 (two), 1:1 and 2:1. A concentration effect and a slow rate of formation suggested that the 1:1 complex was dinuclear. Although useful information about the relative concentrations of these complexes has been obtained from Job curves there is still a lack of solid thermodynamic data such as stability constants and enthalpy and entropy changes. Further, there is disagreement about the composition of the major complexes. For example, Cervilla *et al.*,[2] also applying proton NMR spectroscopy in addition to polarimetric and cryoscopic measurements, preferred to formulate the 1:2 complexes identified by Gil *et al.* as 2:2 species.

The occurrence of protonated forms of different types of complexes can lead, depending on the conditions, to strong overlap of their stability regions. Knowledge about species distributions, based on reliable formation constants for all complexes, is therefore essential and ought to provide the necessary insight to resolve conflicting interpretations of experimental results obtained under diverse conditions.

In this paper we report the results of a potentiometric and enthalpimetric investigation of the complexation of tungstate with malate. A reaction model and set of equilibrium constants have been established which give a satisfactory description of the complexation behaviour under different conditions. Using these results the change in concentration of various complexes could be directly correlated with some experimental measurements previously reported.[1,2] The reaction model also served as a basis for a calorimetric investigation of the system and the determination of the enthalpy and entropy changes of the complexes.

Experimental

Reagents and solutions

All reagents were of analytical grade (Merck, BDH, Aldrich) and solutions were prepared with water obtained from a Millipore Milli-Q system. Sodium tungstate stock solution was prepared from the recrystallized salt $\mathrm{Na_2[WO_4]\cdot 2H_2O}$ and standardized gravimetrically as described previously.[3] Hydrochloric acid was standardized indirectly against potassium hydrogenphthalate by titration with sodium hydroxide. Sodium chloride was purified as described previously.[4] DL-Malic acid was used as received but its purity was checked by titration with sodium hydroxide. Malate solutions were prepared by accurate neutralization of malic acid.

Potentiometric titrations

Mixtures of sodium tungstate and sodium malate (80 $\mathrm{cm^3}$) were titrated with hydrochloric acid at 25 °C using either a Metrohm 636 Titroprocessor or a Metrohm Dosimat. All solutions were made 1.0 mol $\mathrm{dm^{-3}}$ 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 $\mathrm{dm^{-3}}$ NaCl and then bubbled slowly through the titration solution. The initial concentrations (mol $\mathrm{dm^{-3}}$) of tungstate and malate were as follows: 0.01, 0.01; 0.01, 0.02; 0.01, 0.03; 0.01, 0.05; and 0.05, 0.10 thus obtaining solutions with equal concentrations of tungstate and malate or an excess of malate. The $\mathrm{pH_c}$ range covered was 8.5–1.5. In the case of the titration pertaining to equal concentrations of tungstate and malate (0.01 mol $\mathrm{dm^{-3}}$) only data for $\mathrm{pH_c} > 4$ were used because preliminary calculations indicated the presence of higher than 7% isopolytungstate ions at lower $\mathrm{pH_c}$. Titrations were carried out in duplicate and the final computer treatment was based on about 560 data points.

The free hydrogen-ion concentration, h, was determined by measuring the potential, E°, to ±0.2 mV using a Ross combination electrode (Orion 8102 SC) with a 3.0 mol $\mathrm{dm^{-3}}$ KCl bridge solution. Equation (1) was used to calculate h from the meas-

$$E = E^\circ + 59.16 \log h + E_\mathrm{j} \qquad (1)$$

ured potential at each titration point. Values for E° and E_j (the liquid-junction potential) were determined from titrations of 1.0 mol dm^{-3} NaCl with HCl as described by Rossotti.[5] For brevity $-\log h$ is denoted by pH$_c$.

Calorimetric titrations

An isothermal calorimeter, Tronac model 1250, was used for the enthalpy measurements. Solutions containing tungstate and malate (25.0 or 20.0 cm^3) were titrated with 1.0 mol dm^{-3} hydrochloric acid from a precision microburette (2.5 cm^3). The initial concentrations (mol dm^{-3}) of tungstate and malate were as follows: 0.02, 0.04; 0.02, 0.15; 0.10, 0.10. Although the concentrations of the latter titration are rather high the pH$_c$ of the solution after the addition of 2.0 cm^3 acid is only 7.3 and polytungstate ions are therefore absent. In the case of the seven-fold excess of malate an additional titration was done with a solution that already contained some acid (0.01 mol dm^{-3}) in order to cover the low pH$_c$ range. All titrations were done in duplicate and the data were collected automatically by means of a personal computer using software supplied by Tronac. Again, all solutions were made 1.0 mol dm^{-3} with respect to chloride by addition of the appropriate amount of recrystallized sodium chloride. The data were corrected for the endothermic heat of dilution of hydrochloric acid titrated into sodium chloride by using results of previous blank titrations.[6]

Results and Discussion

Potentiometric investigation

The various protonation, condensation and complexation reactions that can take place when a solution containing tungstate and malate is acidified are represented by the general equation (2). The malate anion is formulated as Hmal^{2-} to show the

$$pWO_4^{2-} + qHmal^{2-} + rH^+ \rightleftharpoons [complex]^{(2p+2q-r)-} \quad (2)$$

proton of the α-hydroxyl group which (in the pH range in question) is released only when complexation takes place. Overall formation constants are denoted by β_{pqr} in accordance with the description of species in terms of the stoichiometric coefficients of the reactants, for example, [0,1,2] for malic acid; thus $\beta_{012} = [H_3mal]/[Hmal^{2-}][H^+]^2$.

The results of some representative titrations of malate and of mixtures of tungstate and malate with hydrochloric acid are shown in Fig. 1 as plots of F against pH$_c$. The function F [equation (3)] represents the fraction of the total negative charge

$$F = (H - h)/(2B + 2C) \quad (3)$$

neutralized due to protonation where H, B and C are the analytical concentrations of acid, tungstate and malate respectively. An F value of 1.0 therefore indicates an average charge of zero for the species in solution. For a solution containing only malate species $F \approx 0.98$ at pH$_c \approx 1.5$ indicating almost complete protonation to H$_3$mal (Fig. 1). The F *vs.* pH$_c$ curves for mixtures of tungstate show how protonation is affected by complexation. The curve for an equimolar solution (0.01 mol dm^{-3}) of tungstate and malate represents complete complexation with no excess of either reagent and shows an inflexion at $F \approx 0.5$. This value indicates the presence of a complex with (p,q,r) stoichiometry of $[1,1,2]^{2-}$ and/or $[2,2,4]^{4-}$. At low pH$_c$ the F values show that protonation of the complexes is more difficult than protonation of malate itself, and that these complexes are still anionic.

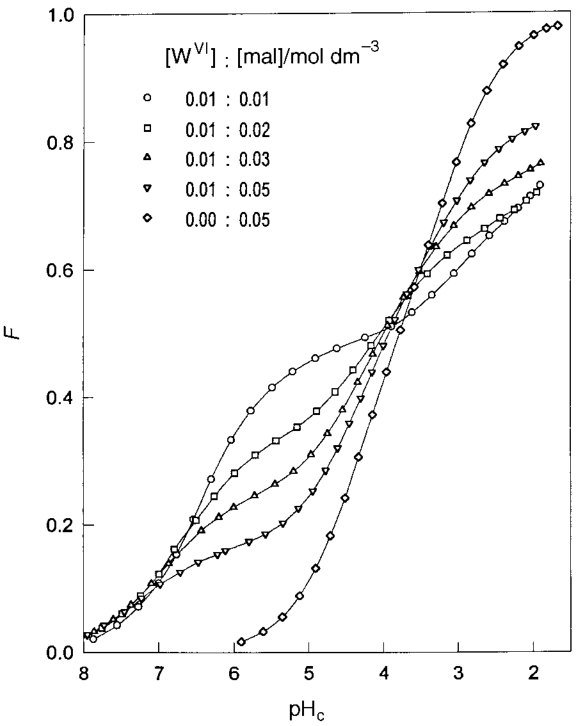


Fig. 1 Plots of function F *versus* pH$_c$ for some representative potentiometric titrations

In the absence of complexation agents acidification of tungstate results in slow reactions at $F \gtrsim 0.6$. An excess of tungstate could therefore not be used in the experiments. Even for equal concentrations of tungstate and malate the concentrations had to be as low as 0.01 mol dm^{-3} to exclude these slow reactions. At $F < 0.6$ for tungstate the presence of small amounts of the polyanions $[W_6O_{20}(OH)_2]^{6-}$, $[W_7O_{24}]^{6-}$, $[HW_7O_{24}]^{5-}$ and $[H_2W_{12}O_{42}]^{10-}$ could be taken into account using previously reported equilibrium constants pertaining to the ionic medium 1 mol dm^{-3} NaCl.[7] However, even at the low equimolar concentration of 0.01 mol dm^{-3} preliminary calculations showed that from pH$_c$ 4 to 2 the percentage concentration of tungstate present as polyanions would increase from about 7 to more than 50%. For this titration, data pertaining to pH$_c$ < 4 were neglected in the calculations. The effect of the presence of the polyanions can also be seen from the shape of this particular F curve which differs from the others in the pH$_c$ region < 3. To account for the protonation of free malate species, previously determined values for the equilibrium constants in 1.0 mol dm^{-3} NaCl were used.[8]

Model testing was done with the program SUPERQUAD.[9] On account of our previous experience with systems of this type all possible complex species with $p = 1$ to 4 and having reasonable q and r values have been considered in the calculations to find the ‘best’ reaction model. The program automatically rejects species for which the relative standard deviation of the formation constant is greater than 33% (or $3\sigma > 0.43$ log units). The final model comprises eleven species of which only the $[2,1,3]^{4-}$ and $[4,4,11]^{5-}$ have standard deviations of greater than 8%, actually 23 and 12% respectively. These species occur in very low percentage concentrations under the conditions employed. Higher concentrations of the reagents, and also an excess of tungstate as required by the stoichiometry of $[2,1,3]^{3-}$, would however not be feasible. The value for the sample standard deviation,[9] $s = 1.24$, based on errors of 0.01 cm^3 in the volume and 0.002 in the pH$_c$ implies a very good fit. The distribution of the complexes as a function of pH$_c$ at concentrations chosen to illustrate the stability regions are shown in Figs. 2 and 3.

The tungstate : malate stoichiometry of the complexes is typical of those previously observed for other comparable tungsten– and molybdenum–ligand systems.[8,10] In particular, the model does not differ much from that obtained for molybdenum(VI) with malate as ligand.[8] However, the tungsten complexes are more stable than the analogous molybdenum com-

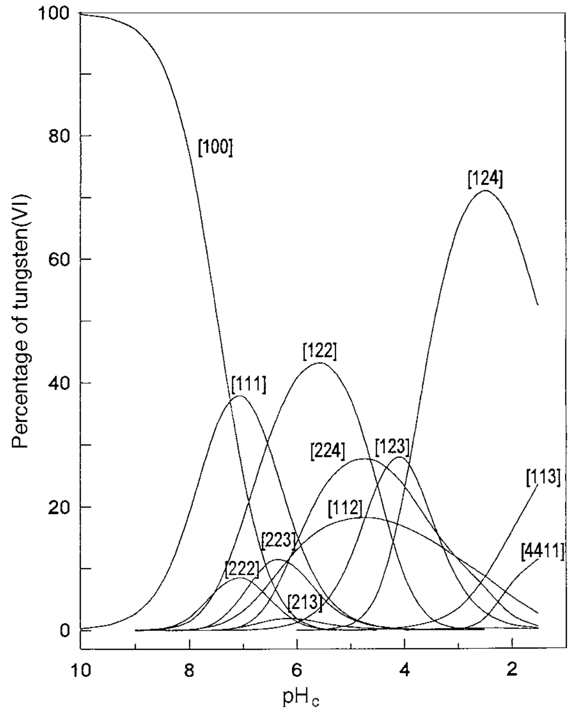


Fig. 2 Distribution of species in the tungsten(VI)–malate system as a function of pH$_c$. Total concentrations of tungstate and malate are 0.02 and 0.04 mol dm^{-3}, respectively

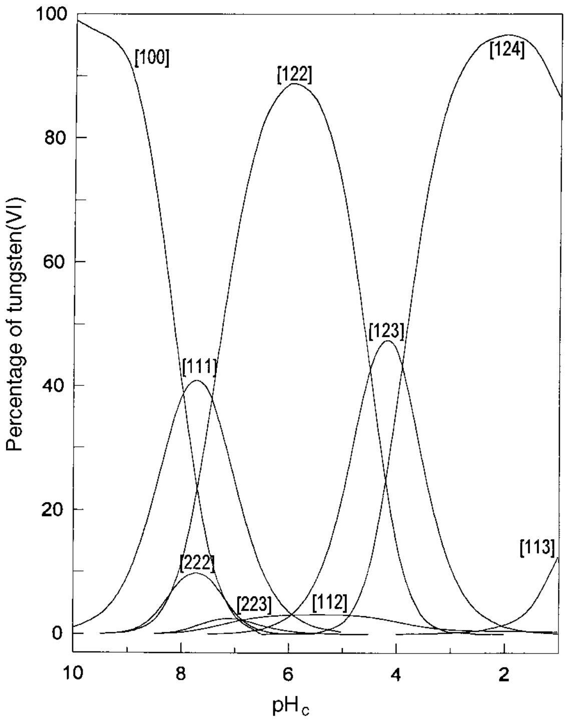


Fig. 3 Distribution of species in the tungsten(VI)–malate system as a function of pH$_c$. Total concentrations of tungstate and malate are 0.02 and 0.15 mol dm^{-3}, respectively

Table 1 Values of the formation constants and other thermodynamic quantities (kJ mol^{-1}) for tungsten(VI)–malate complexes and some molybdenum(VI)–malate[8] complexes in 1 mol dm^{-3} NaCl at 25 °C

Complex [*p*,*q*,*r*]	log β_{pqr} ± 3σ	Δ*G*°/ kJ mol^{-1}	Δ*H*°/ kJ mol^{-1}	*T*Δ*S*°/ kJ mol^{-1}
Tungsten(VI)				
$[1,1,1]^{3-}$	8.85 ± 0.01	−50.5	−64.1 ± 0.3	−13.6
$[1,1,2]^{2-}$	14.78 ± 0.06	−84.4	(−65)*	(19)*
$[1,1,3]^{-}$	17.26 ± 0.03	−98.5	−67 ± 2	32
$[1,2,2]^{4-}$	17.20 ± 0.01	−98.2	−86.0 ± 0.2	12.2
$[1,2,3]^{3-}$	21.70 ± 0.02	−123.9	−91.8 ± 0.5	32.1
$[1,2,4]^{2-}$	25.61 ± 0.01	−146.2	−90.6 ± 0.6	55.6
$[2,1,3]^{3-}$	23.07 ± 0.33	−131.7	—	—
$[2,2,2]^{6-}$	18.87 ± 0.06	−107.7	−115 ± 2	−7
$[2,2,3]^{5-}$	25.72 ± 0.10	−146.8	−121 ± 2	26
$[2,2,4]^{4-}$	31.88 ± 0.07	−182.0	−120 ± 2	62
$[4,4,11]^{5-}$	73.60 ± 0.15	−420.1	−240 ± 20	180
Molybdenum(VI)[8]				
$[1,1,1]^{3-}$	7.47 ± 0.01	−42.6	−47.9 ± 0.4	−5.3
$[1,1,2]^{2-}$	13.23 ± 0.01	−75.5	−55.5 ± 1.2	20
$[1,1,3]^{-}$	15.87 ± 0.08	−90.6	−57 ± 4	33
$[1,2,2]^{4-}$	15.48 ± 0.01	−88.4	−77.0 ± 0.2	11.4
$[1,2,3]^{3-}$	20.13 ± 0.01	−114.9	−83 ± 1	32
$[1,2,4]^{2-}$	24.14 ± 0.01	−137.8	−85.6 ± 0.8	52
$[2,1,3]^{3-}$	20.10 ± 0.04	−114.7	−75 ± 4	40
$[2,2,4]^{4-}$	28.06 ± 0.03	−160.2	−85 ± 10	75
$[4,4,11]^{5-}$	69.92 ± 0.09	−399.1	−221 ± 14	178

* Values in parentheses are approximate.

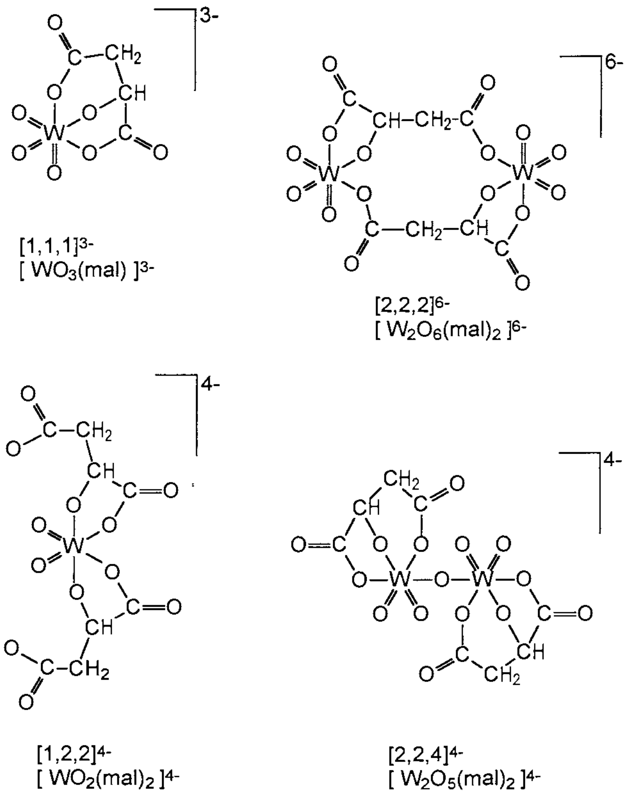
plexes, *e.g.* the difference in the values of the formation constants of the 1 : 1 complexes is in each case about 1.4 log units (Table 1); in the case of the three 1 : 2 complexes the differences are 1.7, 1.6 and 1.5 respectively. These differences in stability are mainly derived from the more favourable enthalpy changes for the tungsten(VI) complexes (*cf.* next section).

Classified in terms of tungsten–malate stoichiometry there are five different types of complexes protonated to various extents. With the exception of the 4 : 4 type, salts of the molybdenum analogues of all types have been isolated in the solid state either as malate or citrate complexes (H_4cit = citric acid = 3-carboxy-3-hydroxypentane-1,5-dioic acid). Thus, salts of the $[1,2,2]^{4-}$, $[1,2,3]^{3-}$ and $[1,2,4]^{2-}$ malate complexes have been prepared,[11] *e.g.* $Cs_4[MoO_2(mal)_2]\cdot 2.5H_2O$, $[NH_4]_3[MoO_2H(mal)_2]\cdot H_2O$ and $Cs_2[MoO_2(Hmal)_2]\cdot H_2O$. A 2 : 2 citrate complex of tungsten(VI), $Na_6[W_2O_5(cit)_2]\cdot 10H_2O$, has been isolated and structurally characterized by X-ray analysis.[12] Citrate complexes of molybdenum[13] which have been obtained by precipitation from aqueous solution and have stoichiometries which correspond with those of malate complexes now identified are potassium salts of $[1,1,1]^{4-}$, $[2,2,4]^{6-}$ and $[2,2,6]^{4-}$. These complexes have been characterized by chemical analysis and various other methods.

If tridentate co-ordination of malate, similar to that of citrate,[10,12] is assumed, structures with five- and six-membered rings with tungsten will be formed as shown in Scheme 1 for the 1 : 1 and 2 : 2 type of complexes. Tridentate co-ordination is expected to have a stabilizing effect on these complexes allowing them to compete successfully with the [1,2,*r*] complexes under suitable conditions. The typical behaviour of α-hydroxycarboxylic acids towards tungsten(VI) and molybdenum(VI) is to form particularly stable 1 : 2 rather than 1 : 1 and 2 : 2 complexes. Whereas the $[2,2,4]^{4-}$ complex can be assumed to have a structure similar to that of the crystallized citrate compound[12] (Scheme 1), the $[2,2,2]^{6-}$ and $[2,2,3]^{5-}$ complexes must have different structures because these complexes cannot be formed just by deprotonation of the $[2,2,4]^{4-}$. The structure proposed for the $[2,2,2]^{6-}$ complex differs from that of the $[2,2,4]^{4-}$ in that the tungsten atoms are linked by the two malate ligands and not by a single oxygen bridge.

One might have expected a $[4,2,8]^{4-}$ complex similar to that identified in molybdenum(VI)–malate[8] and –citrate[10] solutions and also obtained in the solid state by several authors.[14–17] As dictated by the stoichiometry, however, an excess of tungstate would be needed and a rather low pH to form this complex, requirements which cannot be met for this system as discussed above.

The reaction model established and the available formation constants can now be employed to calculate the distribution of



Scheme 1 Proposed structures of some complexes of tungsten(VI) and malate

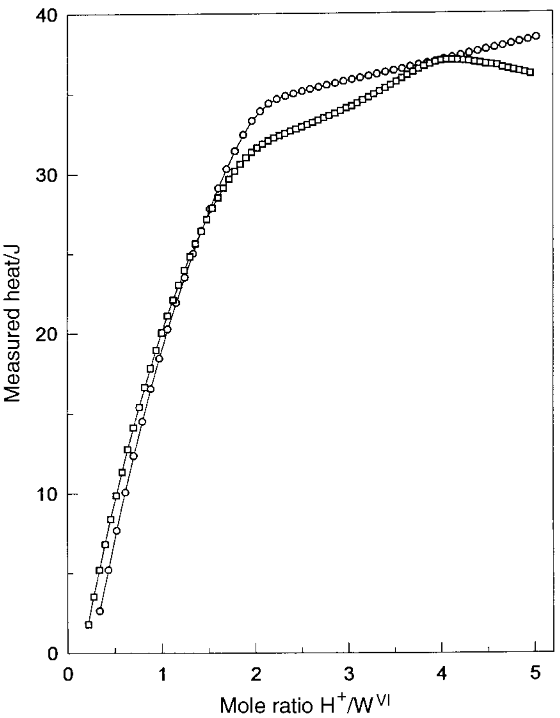


Fig. 4 Measured heat as a function of the molar ratio of acid to tungstate for titrations of the following solutions ([W^{VI}]:[mal]) with hydrochloric acid: 0.02:0.04 (□) and 0.02:0.15 mol dm^{-3} (○)

species in solutions employed in previous investigations. Of particular interest is the work of Gil *et al.*[1] and Cervilla *et al.*[2] where interpretations regarding the stoichiometry of major complexes differed. Comparison of results where these authors conducted measurements on solutions having a large excess of tungstate is obviously not meaningful, but all other results are found to be compatible with the present reaction model. The Job curves constructed from NMR data by Gil *et al.*[1] at pH 3.0, 4.3 and 5.5 show a 1:1, a 2:1 and two 1:2 complexes. Depending on the pH chosen, our calculations show that the 1:2 complexes are the $[1,2,2]^{4-}$, $[1,2,3]^{3-}$ and $[1,2,4]^{2-}$ now identified; the peaks of the Job curves coincide in each case with the maximum concentration of the particular complex. The 1:1 complex shown by the authors to be concentration dependent and for which a 2:2 stoichiometry was suggested corresponds with the $[2,2,4]^{4-}$. They also found indications of a 2:1 species which can be associated with the $[2,1,3]^{3-}$ complex, but in view of the high concentrations used (and excess of tungstate) it could just as well be a $[4,2,8]^{4-}$ complex analogous to the molybdenum complex isolated in the solid state.[17]

The polarimetric measurements by Cervilla *et al.*[2] clearly showed the difference in optical activity of solutions when either malate or tungstate is in excess (actually twenty-fold). With malate in excess the change in optical activity with pH as reported by these authors correlates well with the distribution of the $[1,1,1]^{3-}$, $[1,2,2]^{4-}$ and $[1,2,4]^{2-}$ complexes (*cf.* for example Fig. 3); due to considerable overlap of stability regions of the complexes it is not surprising that their *D vs.* pH curve does not show an inflexion at the pH where the $[1,2,3]^{3-}$ occurs in maximum concentration. The interpretation of this curve by these authors in terms of the formation of only one 1:2 but two 2:2 complexes can not therefore be accepted which also implies that the interpretations of Gil *et al.*[1] regarding the existence of 1:2 complexes were correct. However, it is now clear that the 1:1 complex of Cervilla *et al.*,[2] which occurs at high pH, is indeed a $[1,1,1]^{3-}$ complex and therefore different from the 1:1 complexes of Gil *et al.* which are in fact dimers. The existence of dimeric complexes in solutions with an excess of tungstate has also been postulated by Cervilla *et al.*[2] The present reaction model therefore accommodates quite well the experimental data of these two research groups and successfully resolves the conflicting interpretations.

Enthalpimetric investigation

The results of two representative enthalpimetric titrations are shown in Fig. 4 where the total amount of heat measured, *Q*, is plotted against the molar ratio of acid added to tungstate. (The curves do not start at the origin because the enthalpy of the first few data points, before a steady state is reached, are not included.) The different shapes of the two curves at the same tungstate concentration but with different malate concentrations reflect the change in relative concentrations of the complexes. Above a 1:1 mole ratio of acid to tungstate less heat is developed in the solution having a smaller excess of malate because of the lower percentage of [1,2,*r*] complexes which have (as the calculation will show) the most favourable $\Delta H°$ values. From mole ratio 4 to 5:1, which corresponds to a pH change from 2.9 to 2, this curve shows that the conversion of the $[1,2,4]^{2-}$ complex into the $[1,1,3]^{-}$ and $[4,4,11]^{5-}$ complexes is an endothermic process. For the solution with the greater excess of malate (7.5-fold) the [1,2,*r*] species dominate (*cf.* Fig. 3) and in keeping with this complete conversion into the $[1,2,2]^{4-}$ complex is indicated by a distinct break in the curve occurring at a tungstate:acid mole ratio of 1:2 (Fig. 4).

The enthalpy changes for the formation of the complexes were calculated from the measured heat, *Q*, corrected for dilution effects [equation (4)] where n_{pqr} is the number of moles

$$Q = \Sigma n_{pqr} \Delta H°_{pqr} \qquad (4)$$

formed and $\Delta H°_{pqr}$ the molar enthalpy change of a given species [*p*,*q*,*r*] at 25 °C in 1.0 mol dm^{-3} (Na)Cl medium. The set of linear equations obtained from corresponding *Q* and n_{pqr} values were solved for the unknown $\Delta H°_{pqr}$ parameters using a BMDP least-squares program.[18]

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 (5)–(7) where *b*, *c* and *h* are the

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

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

$$H = h + \Sigma r\beta_{pqr}b^p c^q h^r \qquad (7)$$

equilibrium concentrations of $[WO_4]^{2-}$, $Hmal^{2-}$ and H^+ respectively. The enthalpy changes for the protonation of $Hmal^{2-}$ in 1 mol dm^{-3} NaCl, $\Delta H°_{011} = -2.0$ kJ mol^{-1} and $\Delta H°_{012} = -6.5$ kJ mol^{-1}, determined previously[8] were treated as fixed parameters in the calculation of the $\Delta H°_{pqr}$ values of the complexes.

The concentration of the $[2,1,3]^{3-}$ complex is too small under the experimental conditions to attempt calculation of its enthalpy change and it was therefore neglected. Owing to the strong correlation between the concentrations of the $[1,1,2]^{2-}$ and $[2,2,4]^{4-}$ complexes, entirely independent values for their $\Delta H°$ values could not be calculated: the enthalpy change of the $[1,1,2]^{2-}$ complex, which is present at much lower concentration than the $[2,2,4]^{4-}$, was fixed at a reasonable value, *i.e.* between the values of the $[1,1,1]^{3-}$ and $[1,1,3]^{-}$ complexes, and $\Delta H°$ values for all the other complexes were calculated. The results are given in Table 1.

The quite favourable enthalpy change for complexation is typical for tungstate and is the result of an increase in co-ordination number of tungsten from four to six. When the thermodynamic quantities of the tungsten–malate complexes are compared with those of analogous molybdenum complexes[8] it is seen that the tungsten complexes are in each case more stable and that the major contribution comes from the enthalpy change. For example, the three 1:2 complexes of tungsten and molybdenum have very similar $T\Delta S°$ values, but the $\Delta H°$ values are significantly more favourable in the case of tungsten. This difference clearly illustrates the greater tendency of tungsten(VI) to expand its co-ordination number from four to six.

Also noteworthy is the contribution of the enthalpy change to the greater stability of the 1:2 complexes compared to that of the other complexes; for the 1:2 complexes the enthalpy change is about 25 kJ mol^{-1} (per W atom) more favourable than for the other complexes. The difference in enthalpy change can be explained in terms of the different structures. For example, the $[1,2,2]^{4-}$ complex in comparison with the $[1,1,1]^{3-}$ gains in stability because of the formation of two stable five-membered rings as against one five- and one six-membered ring in the $[1,1,1]^{3-}$ complex. Also to be considered is the enthalpy cost involved in the ionization of the alcoholic proton of malate in the formation of the 1:1 complex, but which can be regained (with profit) *via* liberation of a water molecule when two ligands are co-ordinated to form the $[1,2,2]^{4-}$ complex. The prominence of 1:2 complexes in the case of α-hydroxycarboxylic acids has been noted in previous papers and especially for monocarboxylates such as lactate and mandelate $[PhCH(OH)CO_2^{-}]$.[19,20]

Conclusion

Depending on the concentration of tungstate and malate several complexes occur in varying quantities in the range pH_c 1.5–7.5. Complexes with five different stoichiometric ratios of tungstate to malate have been identified, namely 1:1, 1:2, 2:2, 2:1 and 4:4. These stoichiometries are similar to those of molybdenum malate complexes previously reported.[8] The complexes can be described as follows: the mononuclear complexes $[WO_3(mal)]^{3-}$ and $[WO_2(mal)_2]^{4-}$ and their protonated forms, the different dinuclear complexes $[W_2O_6(mal)_2]^{6-}$, $[W_2O_5(OH)(mal)_2]^{5-}$, $[W_2O_5(mal)_2]^{4-}$, $[W_2O_6(mal)(H_2O)_2]^{3-}$ and finally the tetranuclear complex $[Mo_4O_{10}(OH)(Hmal)_4]^{5-}$. The stoichiometries of complexes which were previously reported only in terms of tungstate:malate ratios have now been fully determined. The formation constants have been used to calculate the concentrations of complexes under various conditions; this information facilitated unambiguous interpretation of experimental work of some earlier investigations and helped to resolve contradictory conclusions. Thermodynamic quantities for the complexes have been determined and compared with those previously reported for the molybdenum–malate complexes.

Acknowledgements

Financial support by the Foundation of Research Development and the University of Stellenbosch is gratefully acknowledged.

References

1 V. M. S. Gil, M. E. T. L. Saraiva, M. M. Caldeira and A. M. D. Pereira, *J. Inorg. Nucl. Chem.*, 1980, **42**, 389 and refs. therein.

2 A. Cervilla, J. A. Ramírez and E. Llopis, *Can. J. Chem.*, 1985, **63**, 1041.

3 J. J. Cruywagen, L. Krüger and E. A. Rohwer, *J. Chem. Soc., Dalton Trans.*, 1991, 1727.

4 J. J. Cruywagen, J. B. B. Heyns and R. F. van de Water, *J. Chem. Soc., Dalton Trans.*, 1986, 1857.

5 H. S. Rossotti, *Talanta*, 1974, **21**, 809.

6 J. J. Cruywagen, J. B. B. Heyns and E. A. Rohwer, *J. Chem. Soc., Dalton Trans.*, 1990, 1951.

7 J. J. Cruywagen and I. F. J. van der Merwe, *J. Chem. Soc., Dalton Trans.*, 1987, 1701.

8 J. J. Cruywagen, E. A. Rohwer and R. F. van de Water, *Polyhedron*, 1997, **16**, 243.

9 P. Gans, A. Sabatini and A. Vacca, *J. Chem. Soc., Dalton Trans.*, 1985, 1195.

10 J. J. Cruywagen, E. A. Rohwer and G. F. S. Wessels, *Polyhedron*, 1995, **14**, 3481 and refs. therein.

11 C. B. Knobler, A. J. Wilson, R. N. Hider, I. W. Jensen, B. R. Penfold, W. T. Robinson and C. J. Wilkins, *J. Chem. Soc., Dalton Trans.*, 1983, 1299.

12 J. J. Cruywagen, L. J. Saayman and M. L. Niven, *J. Crystallogr. Spectrosc. Res.*, 1993, **22**, 40.

13 A. Samotus, A. Kanas, M. Dudek, R. Grybos and E. Hodorowicz, *Transition Met. Chem.*, 1991, **16**, 495.

14 J.-E. Berg, S. Brandänge, L. Lindblom and P.-E. Werner, *Acta Chem. Scand., Ser. A*, 1977, **31**, 325.

15 M. A. Porai-Koshits, L. A. Aslanov, G. V. Ivanova and T. V. Polynova, *J. Struct. Chem.* (*Engl. Transl.*), 1968, **9**, 401.

16 Z. Zhao-Hui, Y. Wen-Bin, W. Hui-Lin and T. Khi-Rui, *Chin. J. Struct. Chem.*, 1995, **14**, 255.

17 L. R. Nassimbeni, M. L. Niven, J. J. Cruywagen and J. B. B. Heyns, *J. Crystallogr. Spectrosc. Res.*, 1987, **17**, 373.

18 W. J. Dixon (Editor), *BMDP Statistical Software*, University of California Press, Berkeley, CF, 1981.

19 J. J. Cruywagen and E. A. Rohwer, *J. Chem. Soc., Dalton Trans.*, 1995, 3433.

20 V. M. S. Gil, *Pure Appl. Chem.*, 1989, **61**, 841.

Received 10*th January* 1997; *Paper* 7/00264E