Equilibria and Thermodynamic Quantities for the Reactions of Molybdenum(VI) and Tungsten(VI) with Mandelate (α-Hydroxybenzeneacetate)†

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The complex formation of molybdate and tungstate with mandelate [PhCH(OH)CO_2^-] have been investigated in the range pH_c 7.5–1.5 by potentiometric, spectrophotometric and enthalpimetric titrations at 25 °C in 1.0 mol dm^{-3} NaCl. The potentiometric data were treated with the computer program SUPERQUAD taking into account the side-reactions of molybdate and tungstate with hydrogen ions. For both systems the 'best' reaction model comprises only one major complex and a number of minor complexes. Thermodynamic quantities have been determined for each of the major complexes. For the molybdenum(VI) complex $[MoO_2(C_8H_6O_3)_2]^{2-}$, log β_{122} = 15.93, $\Delta H^\circ = -78.2$ and $T\Delta S^\circ = 12.7$ kJ mol^{-1} respectively and for the tungsten(VI) complex, $[WO_2(C_8H_6O_3)_2]^{2-}$, log β_{122} = 17.59, $\Delta H^\circ = -86.3$ and $T\Delta S^\circ = 14.1$ kJ mol^{-1}. The equilibrium constant and the enthalpy change for the protonation of mandelate have also been determined, log $K = 3.15$ and $\Delta H = -0.05$ kJ mol^{-1}. The energetics of complexation is discussed in terms of the thermodynamic quantities.

Investigations of the reactions of molybdenum(VI) and tungsten(VI) with different α-hydroxycarboxylates have shown that complexes with various metal-to-ligand ratios, *e.g.* 1 : 1, 2 : 2 and 1 : 2, can occur in solution.[2–5] For those ligands having only one hydroxy and one carboxylic group the preferred stoichiometry appears to be 1 : 2.[2,3,5] Only a few of these complexes have been isolated in the solid state and their structures determined by single-crystal X-ray analysis.[6] Valuable structural information has been obtained on the complexes in solution by NMR analysis and in some cases good estimates of formation constants were deduced.[2,5] However, depending on the co-ordination characteristics of the ligand, quite often series of complexes can occur in successive overlapping equilibria rendering these systems exceedingly complicated.[4] The relative concentrations of the complexes can vary in a complicated manner with variation in pH and/or total concentrations of both metal and ligand. A complete picture of the complexation behaviour under varying conditions can therefore only be established if reliable formation constants are available. Also, the interpretation of calorimetric data depends heavily on the correct quantitative description of the particular system. Previous studies of molybdenum(VI) and tungsten(VI) complexation have shown that systems of this nature can be unravelled by computer treatment of high-quality potentiometric data provided all the side-equilibria with respect to uncomplexed molybdate, tungstate and carboxylate are taken into consideration.[3,4]

We now report the results of a potentiometric, spectrophotometric and calorimetric investigation of the complexation of mandelate [α-hydroxybenzeneacetate, PhCH(OH)CO_2^-] with molybdenum(VI) and tungsten(VI). Mandelate was chosen because of its expected similar co-ordination behaviour towards molybdenum and tungsten when compared to that of lactate [MeCH(OH)CO_2^-]. Lactate forms one major complex with each of these metals, *i.e.* $[MoO_2(C_3H_4O_3)_2]^{2-}$ and $[WO_2(C_3H_4O_3)_2]^{2-}$, as well as several minor complexes.[3] Formation constants for all the complexes have been determined as well as thermodynamic quantities for the major species. No such information is available for mandelate as ligand except for an approximate value (log $K = 14.8 \pm 0.6$) for the formation constant of the molybdenum complex $[MoO_2(C_8H_6O_3)_2]^{2-}$ obtained from NMR data.[5] Several earlier reports indicated the existence of such a 1 : 2 complex for both molybdenum and tungsten.[7] Thermodynamic data for the complexation of these closely related carboxylates with molybdenum and tungsten should be particularly useful because the predominance of a single major species should allow more meaningful comparisons to be drawn than in other relatively complicated systems.

Experimental

Reagents and Solutions.—All reagents were of analytical grade (Merck and BDH) and solutions were prepared with water obtained from a Millipore Milli-Q system. Sodium molybdate and sodium tungstate stock solutions were prepared from the recrystallized salts $Na_2[MoO_4]\cdot 2H_2O$ and $Na_2[WO_4]\cdot 2H_2O$ and standardized gravimetrically as described previously.[8] Hydrochloric acid was standardized indirectly against potassium hydrogenphthalate by titration with sodium hydroxide. Sodium chloride was purified as described previously.[8] Mandelic acid was used as received but its purity was checked by titration with sodium hydroxide. Mandelate solutions were prepared by accurate neutralization of mandelic acid.

Potentiometric Titrations.—Mixtures of sodium molybdate and sodium mandelate (80 cm^3) were titrated (mostly in duplicate) with hydrochloric acid at 25 °C using a Metrohm 636 Titroprocessor. All solutions were made 1.0 mol dm^{-3} with respect to chloride ions by addition of the appropriate amount of recrystallized sodium chloride. To exclude carbon dioxide from the system, a stream of purified nitrogen was passed through 1.0 mol dm^{-3} NaCl and then bubbled slowly through the titration solution. The initial concentrations (mol dm^{-3}) of molybdate and mandelate were as follows: 0.005, 0.05; 0.01, 0.05; 0.01, 0.01; 0.01, 0.005; 0.02, 0.05; 0.05, 0.05 and 0.10, 0.10. The protonation constant of mandelate was determined by titration of a mandelic acid solution (0.05 mol dm^{-3}) with sodium hydroxide. Mixtures of sodium tungstate and sodium mandelate were titrated with hydrochloric acid as described

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above except that a Metrohm Dosimat was used for the addition of the acid. By manually controlling the addition of acid and monitoring the stability of pH readings the absence of slow equilibria can be verified. The initial concentrations (mol dm^{-3}) of tungstate and mandelate were as follows: 0.001, 0.005; 0.005, 0.05; 0.005, 0.015; 0.005, 0.025; 0.01, 0.05; 0.01, 0.025 and 0.02, 0.100.

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

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

measured 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.[9] For brevity, $-\log h$ is denoted by pH$_c$. The value for E_j was found to be $-24.5\ h$ mV and becomes significant only at pH$_c \lesssim 2$.

Spectrophotometric Titrations.—A GBC 920 UV/VIS double-beam spectrophotometer equipped with a Peltier thermocell was used for absorption measurements. The solution in the titration cell, kept in a thermostatted water-bath at 25 °C, was stirred with a non-electric immersion magnetic stirrer. Absorbances were measured in the wavelength range 219–250 nm using quartz cuvettes of path lengths 0.5 and 1.0 cm depending on the concentrations of the solutions; the composition of the reference solution was that of the ionic medium, *i.e.* 1.0 mol dm^{-3} NaCl. The concentrations of molybdate and mandelate in the reaction vessel were 0.2 and 1.0 mmol dm^{-3} for the first titration and 0.02 and 0.8 mmol dm^{-3} for the second. The titrant solution contained in addition to hydrochloric acid and sodium chloride (0.01 and 0.99 mol dm^{-3}) also molybdate and mandelate at the same concentration as those in the test solution. The hydrogen-ion concentration of the solution was measured as described for the potentiometric titrations. Spectra were recorded at pH$_c$ intervals of ≈0.1. A similar titration of mandelic acid (0.08 mmol dm^{-3}) with sodium hydroxide was carried out from which the protonation constant of mandelate was calculated using the program SQUAD.[10] The individual spectra obtained for mandelate and mandelic acid were supplied to the program for the treatment of the absorbance data pertaining to complexation.

Calorimetric Titrations.—An isothermal calorimeter, Tronac model 1250, was used for the enthalpy measurements. Solutions containing molybdate (or tungstate) and mandelate (25.0 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 molybdate (or tungstate) and mandelate were 0.02 and 0.10 mol dm^{-3}.

Separate titrations of mandelate (0.10 mol dm^{-3}) with hydrochloric acid (1.0 mol dm^{-3}) were carried out to determine the heat involved in the protonation of mandelate. All solutions were made 1.0 mol dm^{-3} with respect to chloride by addition of the appropriate amount of recrystallized sodium chloride. A blank titration of acid into sodium chloride was done to correct for the heat of dilution (endothermic) which amounted to ≈1.1% of the heat of complexation per mol of acid added. The heat of protonation of mandelate, however, is so small that it amounts to only about 10% of the heat of dilution. Titrations were carried out in duplicate.

Results and Discussion

Potentiometric Investigation.—The various protonation, condensation and complexation reactions that can take place when a solution of molybdate (or tungstate) and mandelate is acidified are represented by the general equation (2). For brevity, species with overall formation constants β_{pqr} will

$$p[\mathrm{MoO_4}]^{2-} + q\mathrm{PhCH(OH)CO_2}^- + r\mathrm{H}^+ \rightleftharpoons [\mathrm{complex}]^{(2p+q-r)-} \qquad (2)$$

mostly be described in terms of the stoichiometric coefficients of the reactants, for example $[1,0,1]^-$ for hydrogen molybdate. In the treatment of the data all side-equilibria involving the reaction of protons with mandelate, molybdate and tungstate have to be taken into account. The protonation constant of mandelate was determined in separate titrations of mandelic acid with sodium hydroxide. The value obtained, $\log \beta_{011} = 3.15 \pm 0.01$ (error limits 3σ), can be compared with that determined in 1.0 mol dm^{-3} KNO$_3$, namely 3.14 ± 0.01.[11]

For the equilibria involving uncomplexed molybdate the species $[\mathrm{HMoO_4}]^-$, $[\mathrm{MoO_3(H_2O)_3}]$, $[\mathrm{MoO_2(OH)(H_2O)_3}]^+$, $[\mathrm{HMo_2O_7}]^-$, $[\mathrm{Mo_7O_{24}}]^{6-}$, $[\mathrm{HMo_7O_{24}}]^{5-}$, $[\mathrm{H_2Mo_7O_{24}}]^{4-}$, $[\mathrm{H_3Mo_7O_{24}}]^{3-}$, $[\mathrm{Mo_8O_{26}}]^{4-}$ and $[\mathrm{HMo_2O_6}]^+$ were taken into account using previously determined equilibrium constants pertaining to a 1 mol dm^{-3} NaCl medium at 25 °C.[12] In the case of tungstate, acidification up to $Z \approx 1.2$ (Z = degree of protonation) results in the formation of the following polyanions of which formation constants for the conditions in question have been reported,[13] namely $[\mathrm{W_6O_{20}(OH)_2}]^{6-}$, $[\mathrm{W_7O_{24}}]^{6-}$, $[\mathrm{HW_7O_{24}}]^{5-}$ and $[\mathrm{H_2W_{12}O_{42}}]^{10-}$. At $Z \gtrsim 1.2$ slow equilibria occur and conditions were chosen to prevent these reactions, *i.e.* relatively low tungstate concentration and a sufficient excess of mandelate. In the treatment of the data the equilibrium constants of the above species were supplied to the program to check whether the concentrations of polyanions were indeed negligible.

The results of some representative titrations are shown in Figs. 1 and 2 as plots of F against pH$_c$. For these protonation curves the function F represents the fraction of the total negative charge neutralized due to protonation where H, B and C are the analytical concentrations of acid, molybdate (or tungstate) and mandelate [equation (3)]. An F value of 1.0

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

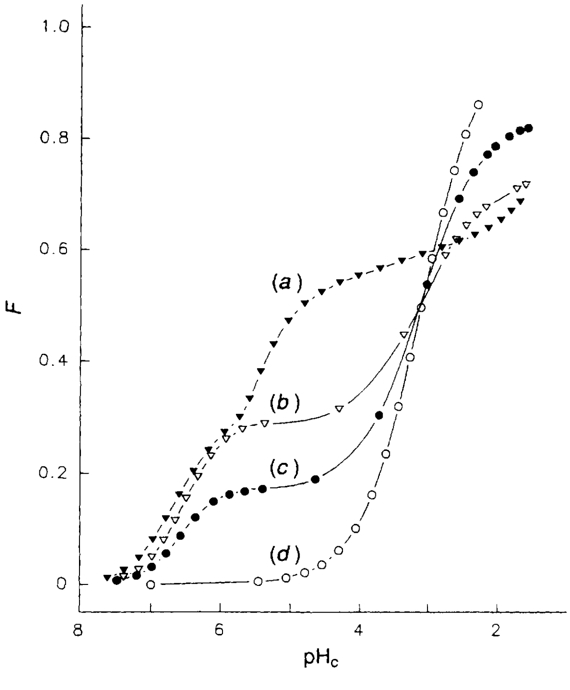

Fig. 1 Plots of function F *versus* pH$_c$ for some representative potentiometric titrations. Initial concentrations (molybdate, mandelate): (*a*) 0.05, 0.05; (*b*) 0.01, 0.05; (*c*) 0.005, 0.05 and (*d*) 0, 0.05 mol dm^{-3}

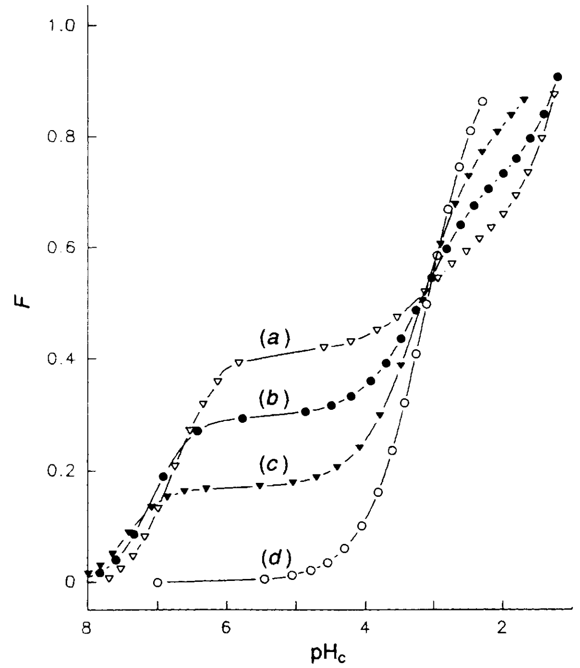

Fig. 2 Plots of function F *versus* pH$_c$ for some representative potentiometric titrations. Initial concentrations (tungstate, mandelate): (*a*) 0.005, 0.015; (*b*) 0.005, 0.025; (*c*) 0.005, 0.05 and (*d*) 0, 0.05 mol dm^{-3}

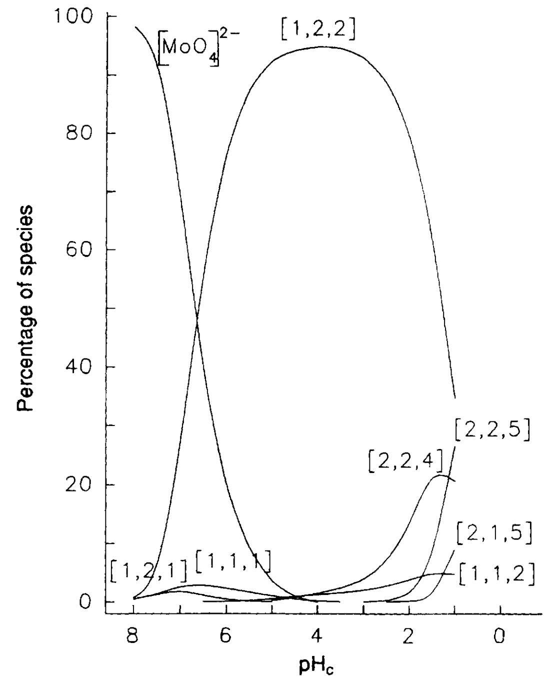

Fig. 3 Distribution of species in the molybdenum(VI)–mandelate system as function of pH$_c$. The total concentrations of molybdate and mandelate are 0.05 and 0.10 mol dm^{-3}, respectively

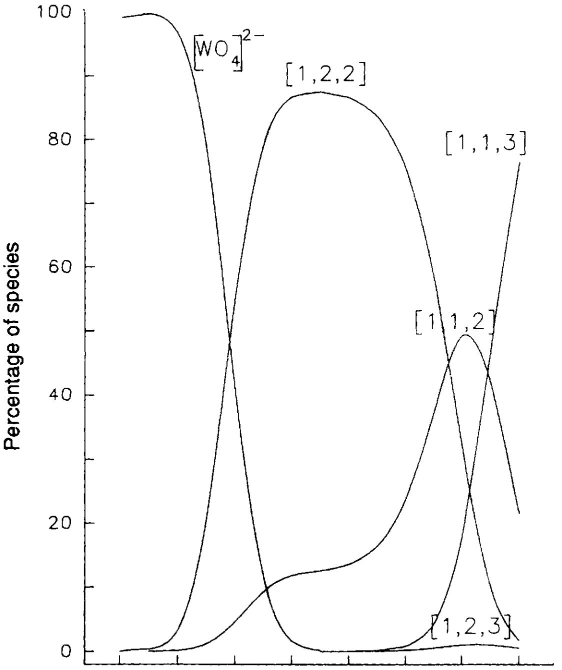

Fig. 4 Distribution of species in the tungsten(VI)–mandelate system as a function of pH$_c$. The total concentrations of tungstate and mandelate are 0.001 and 0.003 mol dm^{-3}, respectively

therefore indicates an average charge of zero for the species in solution, *e.g.* for the formation of mandelic acid. The curves show that the complex-formation characteristics for the two systems are very similar. Complexation starts at pH$_c$ 7–8 resulting in a sharp increase in F values until at low pH$_c$ the protonation of the complexes becomes more difficult than that of mandelate itself. The inflexions exhibited by the curves pertaining to an excess of carboxylate show that after all the molybdate or tungstate has reacted very little protonation takes place until the pH$_c$ is low enough ($\approx$4.5) for free mandelate to become protonated and F increases again.

The potentiometric data were treated with the program SUPERQUAD[14] to find the reaction model that would give the best description for each of the systems. A noticeable feature of the best models is the predominance of the $[1,2,2]^{2-}$ complex over a wide pH$_c$ range. The distribution of the complexes as a function of pH$_c$ at concentrations chosen to illustrate the stability regions are shown in Figs. 3 and 4. A number of minor species also occur in the models (Table 1) of which the $[1,2,1]^{3-}$ and $[1,2,3]^-$ molybdenum complexes and the $[1,2,3]^-$ tungsten complex with relative standard deviations of 20–23% are the most uncertain; the program automatically rejects species for which the relative standard deviation is greater than 33%. In the case of the tungstate system fewer minor species were identified, in particular dinuclear complexes, which would not be expected because of the requirement of low tungstate concentration and excess of mandelate as discussed above.

The models now obtained are, with few exceptions regarding very minor species, the same as those reported for complexation with lactate. When the formation constants for the $[1,2,2]^{2-}$ complexes of molybdenum and tungsten are compared it is seen that the tungsten complex is significantly more stable than the molybdenum complex, the difference being 1.66 and 1.76 log units for the mandelate and lactate complexes respectively. For both molybdenum and tungsten the mandelate complex is only slightly more stable than the lactate complex, the difference between the values of the stability constants being only 0.22 and 0.12 log units respectively. Apart from reflecting the consistency of the results, these small differences show that substituting a phenyl for a methyl group has little effect on the co-ordination strength of these ligands. The structure of the lactate and mandelate complexes should be similar (Fig. 5). Information obtained from NMR spectra for α-hydroxycarboxylic acids[5] indicated that the carboxyl oxygens are *trans* to the terminal oxygens of the *cis*-MoO_2 and -WO_2 units similar to the situation in tartrate, malate and citrate complexes of known structure.[6]

Table 1 Reaction models and formation constants of the various molybdenum(VI) and tungsten(VI) mandelate complexes

Complex	log β_{pqr} ± 3σ	
	Mo^{VI}	W^{VI}
$[1,2,1]^{3-}$	7.80 ± 0.30	—
$[1,2,2]^{2-}$ *	15.93 ± 0.01	17.59 ± 0.01
$[1,2,3]^{-}$	16.27 ± 0.29	18.09 ± 0.30
$[1,1,1]^{2-}$	6.83 ± 0.12	—
$[1,1,2]^{-}$	11.57 ± 0.06	13.78 ± 0.07
$[1,1,3]$	—	15.33 ± 0.07
$[2,2,4]^{2-}$	25.87 ± 0.03	—
$[2,2,5]^{-}$	26.86 ± 0.12	—
$[2,1,3]^{2-}$	19.00 ± 0.15	—
$[2,1,4]^{-}$	21.18 ± 0.24	—
$[2,1,5]$	23.00 ± 0.06	—

* For the corresponding lactate complexes log β_{122} = 15.71 ± 0.01 (Mo^{VI}) and 17.47 ± 0.01 (W^{VI}).

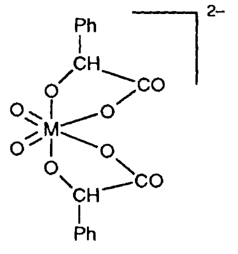

Fig. 5 Probable structure of the $[1,2,2]^{2-}$ complex where M = Mo or W

Spectrophotometric Investigation.—By choosing relatively favourable conditions it ought to be possible to verify the existence of at least the major molybdenum complex by spectrophotometry (in the UV region) despite some of the limitations imposed by the nature of the system. At the very low concentrations required for the absorption measurements at least a four- to five-fold excess of mandelate is essential to promote complex formation. Although the absorption of mandelate is weaker than that of molybdate this excess means that its contribution to the total absorption measured becomes comparable to that of molybdate. Fortunately this contribution does not change much during the titration because of the relatively small difference between the spectra of mandelate and mandelic acid (Fig. 6) which in any case had been accurately determined in a separate titration experiment and could be supplied to the program in the treatment of the data. The protonation constant of mandelate calculated with the program SQUAD from the data of this experiment, log β_{011} = 3.16 ± 0.01 (error limits 3σ), agrees very well with the value (3.15) obtained from the potentiometric data.

Under the conditions of the first titration experiment (0.2 and 1.0 mmol dm^{-3} molybdate and mandelate respectively) a maximum concentration of about 90% of the $[1,2,2]^{2-}$ complex is present over the range pH$_c$ 6–4, with less than 6% of the $[1,1,2]^{-}$ species which had to be neglected in the calculations. The data treated with SQUAD resulted in a good fit between experimental and calculated absorbances with the value of the formation constant of the $[1,2,2]^{2-}$ complex, log β_{122} = 16.01, in very good agreement with that obtained by potentiometry (15.93).

A second titration was done under conditions where a greater percentage of the $[1,1,2]^{-}$ complex (maximum ≈ 25%) would be present while the concentration of other minor complexes can be neglected. However, under these conditions the presence of $[HMoO_4]^{-}$ and in particular $[MoO_3(H_2O)_3]$ at pH$_c$ < 3 reaches concentrations comparable to and greater than that of the $[1,1,2]^{-}$ complex. The spectra and equilibrium constants of these two molybdenum species, known from previous work,[15] were therefore also supplied to the program. The data of the two titrations were combined and in spite of the various uncertainties involved in the procedure the value calculated for the formation constant of the $[1,1,2]^{-}$ complex, log β_{112} = 11.7, agreed reasonably well with that obtained by potentiometry (11.57). The value now calculated for the formation constant of the $[1,2,2]^{2-}$ complex log β_{122} = 16.03 was practically the same as that obtained from the data of the first experiment alone. The spectra of the complexes are shown in Fig. 7. The reaction model proposed for the molybdenum(VI)–mandelate system and the formation constants can therefore be accepted with sufficient confidence to warrant a calorimetric investigation. Owing to the very small part of the UV spectrum of tungstate that is available for absorption measurements a similar spectrophotometric study of tungsten(VI)–mandelate complex formation would not be feasible.

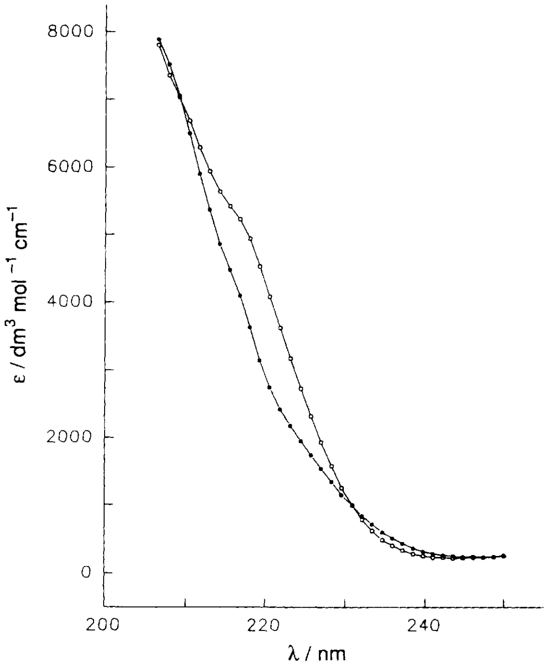

Fig. 6 Absorption spectra of mandelic acid (●) and mandelate (○)

Enthalpimetric Investigation.—The results of the enthalpimetric titrations are shown in Fig. 8 where the total amount of heat measured, Q, is plotted against the molar ratio of acid added to either molybdate or tungstate. The curves show a clear break at a mole ratio of 1:2 which corresponds to the stoichiometry of the major complex $[1,2,2]^{2-}$, determined by potentiometry and spectrophotometry. The heat evolved in the formation of the tungsten complex is greater than that for the molybdenum complex. Included in the measured heat is a very small contribution from the protonation of mandelate which needs to be present in excess to ensure complete complexation and prevent side-reactions of molybdate and tungstate with protons. Also, under the chosen conditions minor complex species do not appear in measurable concentrations for most of the titration which simplifies the calculation of enthalpy changes. To account for the heat involved in the protonation of free mandelate the enthalpy change for the reaction was determined in a separate titration. The value obtained after correcting for the endothermic heat of dilution was $\Delta H^{\circ} = -0.05$ kJ mol^{-1} compared to -1.7 kJ mol^{-1} determined for lactate under the same conditions.[3]

The values obtained for the enthalpy change for the formation of the $[1,2,2]^{2-}$ complexes of tungsten and

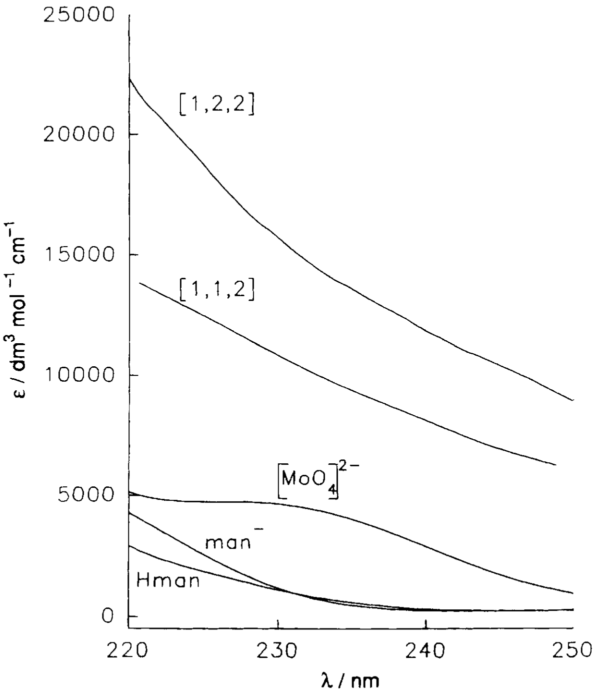

Fig. 7 Absorption spectra of various species in the molybdenum(VI)–mandelic acid (Hman) system

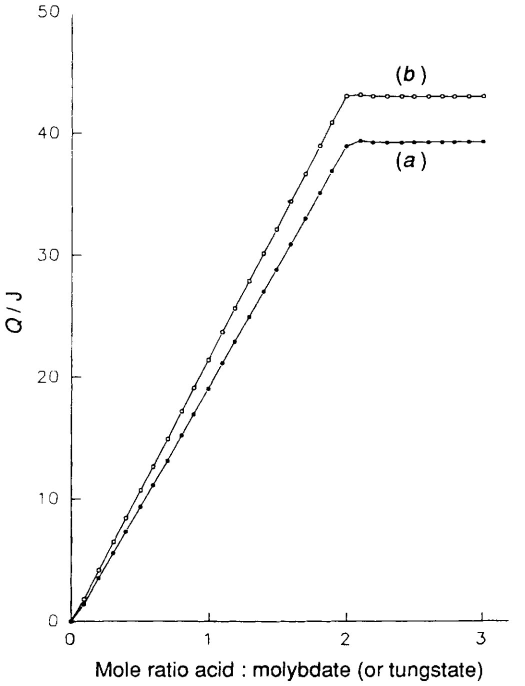

Fig. 8 The measured heat evolved, Q, as a function of the molar ratio of acid to molybdate (a) or tungstate (b) for the titration of 0.1 mol dm^{-3} mandelate and 0.02 mol dm^{-3} molybdate and tungstate, respectively

Table 2 Thermodynamic quantities (kJ mol^{-1}) for complex formation of molybdate and tungstate with mandelate and lactate in 1.0 mol dm^{-3} NaCl at 298.15 K

Mandelate (H_2L)	ΔG°	ΔH°	$T\Delta S^\circ$
$[MoO_2L_2]^{2-}$	−90.93 ± 0.06	−78.2 ± 0.5	12.7 ± 0.5
$[WO_2L_2]^{2-}$	−100.40 ± 0.06	−86.3 ± 0.5	14.1 ± 0.5
HL^-	−17.98 ± 0.03	−0.05 ± 0.5	17.5 ± 0.5
Lactate (H_2L)[3]			
$[MoO_2L_2]^{2-}$	−89.67 ± 0.06	−72 ± 2	18 ± 2
$[WO_2L_2]^{2-}$	−99.72 ± 0.06	−80 ± 2	20 ± 2
HL^-	−20.52 ± 0.02	−1.7 ± 0.2	18.8 ± 0.2

molybdenum are listed in Table 2. That for the tungsten complex is about 8 kJ mol^{-1} more favourable than for the molybdenum. The entropy changes for the two reactions are about the same and compare well with the results previously obtained for complexation with lactate.[3] The enthalpy change therefore is the cause for the greater stability of the tungsten complex and reflects the greater tendency of tungsten to increase its co-ordination number from four to six. This effect is also seen in the greater stability of polyoxoanions of tungsten(VI) compared to those of molybdenum(VI) as has been discussed previously.[3]

The results of this investigation again demonstrate the somewhat special co-ordination behaviour of α-hydroxycarboxylic acid groups towards molybdenum(VI) and tungsten(VI) in that very stable 1 : 2 rather than 1 : 1 metal : ligand complexes are formed. In the case of oxalate, for example, the 1 : 1 complex $[MoO_3(C_2O_4)(H_2O)]^{2-}$ predominates at high pH$_c$.[8] This behaviour has been explained in terms of the energy cost involved in the ionization of the alcoholic proton when a 1 : 1 complex is formed. When a 1 : 2 complex is formed, however, the cost can be regained (with profit) when two protons become available to form a water molecule.

Conclusion

Both molybdenum(VI) and tungsten(VI) form one predominant complex with mandelate, *i.e.* $[MoO_2(C_8H_6O_3)_2]^{2-}$ and $[WO_2(C_8H_6O_3)_2]^{2-}$ as well as several minor complexes. The co-ordination behaviour of mandelate towards these metals is very similar to that of lactate. The tungsten(VI) complexes are more stable than those of molybdenum(VI) due to a more favourable enthalpy change for the complexation reaction (≈8 kJ mol^{-1}) which is associated with the greater tendency of tungsten(VI) to expand its co-ordination sphere from four to six.

Acknowledgements

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