A Potentiometric, Spectrophotometric, and Calorimetric Investigation of Molybdenum(vi)–Oxalate Complex Formation

Johannes J. Cruywagen,* J. Bernard Heyns, and Ronald F. van de Water
Department of Chemistry, University of Stellenbosch, Stellenbosch 7600, South Africa

Complexation between molybdate and oxalate has been investigated in the pH_c range 2.0—7.0 by potentiometric, spectrophotometric, and enthalpimetric titrations at 25 °C in 1.0 mol dm^{-3} sodium chloride. The potentiometric data were treated with the computer program MINIQUAD taking into account side reactions of molybdate and oxalate with hydrogen ions. The 'best' reaction model comprises the three complexes $(1,1,2)^{2-}$, $(2,2,5)^{3-}$, and $(2,2,6)^{2-}$ with formation constants log $\beta_{112} = 13.619$, log $\beta_{225} = 31.20$, and log $\beta_{226} = 34.08$; the numbers in parentheses refer to the values of p, q, and r in the general formula $(MoO_4^{2-})_p(C_2O_4^{2-})_q(H^+)_r$. The spectrophotometric data were treated with the program SQUAD and the results obtained confirmed those obtained by potentiometry. The u.v. spectra of the complexes are reported. The enthalpy and entropy changes for complex formation were calculated from the enthalpimetric data using the values of the now known formation constants. The enthalpy values are: $\Delta H_{112}^{\ominus} = -59.5$, $\Delta H_{225}^{\ominus} = -123.0$, and $\Delta H_{226}^{\ominus} = -117.0$ kJ mol^{-1}. Equilibrium constants for the successive protonation of oxalate in 1 mol dm^{-3} sodium chloride have also been determined, log $\beta_{011} = 3.52$ and log $\beta_{012} = 4.41$.

Complexes with a molybdate to oxalate ratio of 1:1, 1:2, 2:1, and 2:2 have been reported to exist in the solid state as the salts of various monovalent cations.[1-9] Of these compounds the compositions of only the 1:1 and 2:2 types, for which structural data are available, can be regarded as certain, for example $K_2[Mo_2O_5(C_2O_4)_2(H_2O)_2]$ and $[NH_4]_2[MoO_3(C_2O_4)]\cdot H_2O$.[5,6] The isolation of compounds containing the complex anions $[MoO_2(OH)_2(C_2O_4)_2]^{4-}$, $[Mo_2O_5(OH)_2(C_2O_4)_2]^{4-}$, and $[Mo_2O_5(OH)(C_2O_4)_2]^{3-}$, with $[Co(en)_3]^{3+}$ (en = ethylenediamine) as counter ion, have recently been reported by Beltrán et al.[10] They concluded that these complex anions also exist in solution and reported spectrophotometrically determined formation constants. A study of the thermal behaviour of the solids has also been reported.[11]

Results of earlier investigations by various methods have been interpreted mainly in terms of the formation of only one complex with a molybdenum to oxalate ratio of 1:1.[12-16] A recent potentiometric investigation[17] in which the data were subjected to computer treatment showed that only one complex with stoicheiometry corresponding to $MoO_3(C_2O_4)^{2-}$ exists in the pH range 4—7. The results of the latter study contradict the findings of Beltrán et al.[10] concerning the stoicheiometry of the predominant complex in solution.

In this paper we present the results of a comprehensive investigation of molybdenum(vi)–oxalate complex formation in the pH range 2—7. Computer treatment of potentiometric and spectrophotometric data led to the identification of three major complexes in solution and to the determination of their formation constants. The enthalpy and entropy changes for the formation of these complexes have also been determined.

Experimental

Reagents and Solutions.—All reagents were of analytical grade (Merck p.a.) and solutions were prepared with deionised distilled water. Sodium molybdate solution was prepared from recrystallised $Na_2MoO_4\cdot2H_2O$. Sodium chloride was purified as follows. A saturated solution was allowed to stand for a week and then filtered. Relatively large and pure sodium chloride crystals were then obtained by allowing the solution to

evaporate slowly at *ca.* 25 °C for several weeks. Stock solutions prepared from the recrystallised salts were standardised by evaporating known volumes to dryness and heating at 160 °C to constant weight. Hydrochloric acid was standardised by titration with potassium hydrogenphthalate. Sodium oxalate solution was prepared from the recrystallised solid and standardised by titration with potassium permanganate solution.

Potentiometric Measurements.—Titrations were carried out at 25.0 °C with the titration flask in a water-bath starting with mixtures (90 cm^3) of sodium oxalate and sodium molybdate. The initial concentrations (mol dm^{-3}) of molybdate and oxalate titrated with hydrochloric acid were respectively as follows: 0.001, 0.020; 0.001, 0.005; 0.001, 0.001; 0.001, 0.0002; 0.01, 0.04; 0.01, 0.01; 0.01, 0.0025; and 0.05, 0.05. One titration was performed starting with a mixture containing 0.075 mol dm^{-3} hydrochloric acid and 0.05 mol dm^{-3} sodium oxalate and titrating with 0.05 mol dm^{-3} sodium molybdate solution. A total of 214 data points collected from these titrations were used in the computations. All solutions were made 1.0 mol dm^{-3} with respect to chloride 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, which both stirred the solution and excluded carbon dioxide from the system. The free hydrogen ion concentration, h, was determined by measuring the potential (to ±0.2 mV) with a T & C model 1002 research pH meter. A Ross combination electrode (supplied by Orion Research) with a 3 mol dm^{-3} KCl internal filling solution was used. Because of the relatively large volumes used in the experiments contamination by small amounts of potassium ions during a titration could be neglected. The Ross electrode system proved to be very stable showing drifts of $\leqslant0.1$ mV per day. The relationship between the measured potential E (in mV) and the concentration of free hydrogen ions at 25 °C is given by equation (1). Values for E and E_j were determined from

$$E = E^{\ominus} + 59.16 \log h + E_j \qquad (1)$$

titrations of 1.0 mol dm^{-3} NaCl with hydrochloric acid as described by Rossotti.[18] The value of E_j was found to be $-17h$

mV. As the equilibrium hydrogen ion concentration was below 0.01 mol dm^{-3} for most experiments the E_j term had little effect on the measured potential. It was, however, important in the determination of the first dissociation constant of oxalic acid where the hydrogen ion concentration was increased to 0.1 mol dm^{-3}. For brevity, $-\log h$ is denoted by pH_c.

Spectrophotometric Measurements.—All measurements were made with a Varian Cary 210 spectrophotometer. Individual u.v. spectra for $H_2C_2O_4$, $HC_2O_4^-$, and $C_2O_4^{2-}$ in 1 mol dm^{-3} (sodium) chloride medium were obtained by the method previously described.[19]

The molybdenum(VI)–oxalate complex formation equilibria were studied by a titration procedure similar to that used for the potentiometric measurements. Two separate experiments were performed. In the first, a peristaltic pump was used to circulate the reaction mixture from the titration cell to a flow-through cuvette with adjustable path length, set at 0.1 cm (calibrated path 0.102 cm). A portion of sodium molybdate (110 cm³, 9.094×10^{-4} mol dm^{-3}) was titrated with 3.834×10^{-2} mol dm^{-3} oxalic acid; both solutions were 1.0 mol dm^{-3} in NaCl. The total oxalic acid concentration varied from 1.458×10^{-4} to 5.884×10^{-4} mol dm^{-3} (the Mo^{VI} concentration thereby varying from 9.059×10^{-4} to 7.698×10^{-4} mol dm^{-3}) to cover the pH_c range 4.9—2.3 for the recording of spectra. The value of h was calculated from the measured potential, E, of the solution in the titration cell, as described above. The absorbance of the reaction mixture at each of 12 E values was measured, against air as reference, at intervals of 3 nm in the range 210—279 nm. Blank corrections were applied to all spectra by subtraction of the appropriate absorbances obtained for a 1.0 mol dm^{-3} NaCl solution at the same path length.

In the second titration the same experimental set-up was used. However, the titration cell was charged with a solution (100.0 cm³) containing the following analytical concentrations of reagents: 0.005 mol dm^{-3} Na_2MoO_4, 0.006 mol dm^{-3} $H_2C_2O_4$, 0.01 mol dm^{-3} HCl, and 0.99 mol dm^{-3} NaCl. The path length was set at 0.02 cm (calibrated path 0.022 45 cm). This solution was titrated with 0.25 mol dm^{-3} NaOH, also 1.0 mol dm^{-3} in NaCl. The analytical Mo^{VI} concentration varied from 0.005 to 0.004 684 mol dm^{-3}, while that of oxalate varied from 0.006 to 0.005 621 mol dm^{-3}, corresponding to a change in pH_c from 2.1 to 5.1. The corrected absorbances of the reaction mixture were determined at each of seven E values at intervals of 2 nm between 210 and 300 nm, and the value of h calculated as before.
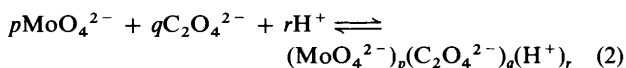
Calorimetric Measurements.—An isothermal titration calorimeter, Tronac model 550, described elsewhere[20,21] was used for the measurements. The titration was carried out in two steps. First, a solution (20.00 cm³) containing sodium molybdate (0.05 mol dm^{-3}), sodium oxalate (0.05 mol dm^{-3}) and sodium chloride (1 mol dm^{-3}) was titrated with 1 mol dm^{-3} HCl from a Gilmont precision microburette (2.5 cm³). The titrant was added at constant speed (0.05 cm³ min^{-1}) and the average number of heat pulses supplied by the control heater (displayed in digital form and printed as counts per second) was obtained at fixed intervals of 100 s.

For the second part of the titration the same solution was further titrated with 1 mol dm^{-3} HCl until *ca.* 4 mmol of the acid had been added. Because of the very small amount of heat involved, the rate of delivery of the titrant was increased to 0.15 cm³ min^{-1} and data points were again recorded at intervals of 100 s.

A blank titration of 1 mol dm^{-3} NaCl with 1 mol dm^{-3} HCl was carried out to correct for the small endothermic heat of dilution; the amount of heat measured varied from 0.50 to 0.34 kJ mol^{-1} in the course of the titration.

Results and Discussion

Potentiometric Investigation.—The equilibria for the various possible complexation, protonation, and condensation reactions can be represented by the general equation (2). For brevity a

$$p\text{MoO}_4^{2-} + q\text{C}_2\text{O}_4^{2-} + r\text{H}^+ \rightleftharpoons$$
$$(\text{MoO}_4^{2-})_p(\text{C}_2\text{O}_4^{2-})_q(\text{H}^+)_r \quad (2)$$

species with overall formation constant β_{pqr} is denoted by the stoicheiometric coefficients which define its composition, *i.e.*, $(p,q,r)^{(2p+2q-r)-}$.

To create conditions that would be favourable for the formation of complexes with stoicheiometry corresponding to either $p > q$ or $p < q$, some titrations were done with one of the reactants in large excess. It was, therefore, important to consider all side reactions of uncomplexed molybdate and oxalate in the computer treatment of the data. The molybdenum(VI) species HMoO_4^-, Mo(OH)_6, $\text{Mo}_7\text{O}_{24}^{6-}$, $\text{HMo}_7\text{O}_{24}^{5-}$, $\text{H}_2\text{Mo}_7\text{O}_{24}^{4-}$, and $\text{Mo}_8\text{O}_{26}^{4-}$ were taken into account using previously determined equilibrium constants pertaining to 1 mol dm^{-3} NaCl medium at 25 °C.[22]

Equilibrium constants for the protonation of oxalate in 1 mol dm^{-3} NaCl were determined in a separate potentiometric titration as described previously.[19] The values obtained, $\log \beta_{011} = 3.52 \pm 0.02$ and $\log \beta_{012} = 4.41 \pm 0.02$ (error limits 3σ) can be compared with those reported[23] for 1 mol dm^{-3} $NaClO_4$, namely $\log \beta_{011} = 3.55$ and $\log \beta_{012} = 4.56$.

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

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

total analytical concentrations of hydrochloric acid, molybdate and oxalate respectively. The inflexions shown by curves 1 and 2 (Figure 1) at $pH_c \sim 4$ indicate the existence of a predominant complex with $F = 0.5$, which corresponds to a stoicheiometry of $(1,1,2)^{2-}$. The different value of F at which the inflexion of curve 5 occurs, however, does not mean that another complex of different stoicheiometry has been formed at $pH_c \sim 4$. The smaller F value is only the result of the presence of an excess of uncomplexed oxalate which has a much lower tendency to take up protons than the complexed species, as can be seen from the difference between the protonation curve for oxalate and the other curves.

The potentiometric data were treated with the computer program MINIQUAD[24] to examine various reaction models and thereby characterise the complexes in terms of their stoicheiometry and stability constants. In the search for the 'correct' model the error square sum was taken as first criterion, but in the final selection a complex was considered acceptable only if the value of its formation constant was greater than three times that of the standard deviation. A standard deviation of 33.3% corresponds to 0.145 (or 0.43 for 3σ) when expressed in logarithmic form.

In view of previous work both mono- and di-nuclear complexes, co-ordinated with either one or two oxalates, had to be considered as possibilities. A reasonable starting point was, therefore, species with molybdate to oxalate ratios of $1:1$, $1:2$, and $2:2$ with two protons for each co-ordinated oxalate, *i.e.* the complexes $(1,1,2)^{2-}$, $(1,2,4)^{2-}$, and $(2,2,4)^{4-}$ corresponding to F values of 0.5, 0.666, and 0.5 respectively. The first run indicated the existence of a $(1,1,2)^{2-}$ species as could be expected from the prominent inflexions shown by the formation curves; the standard deviation of the equilibrium constant was quite small
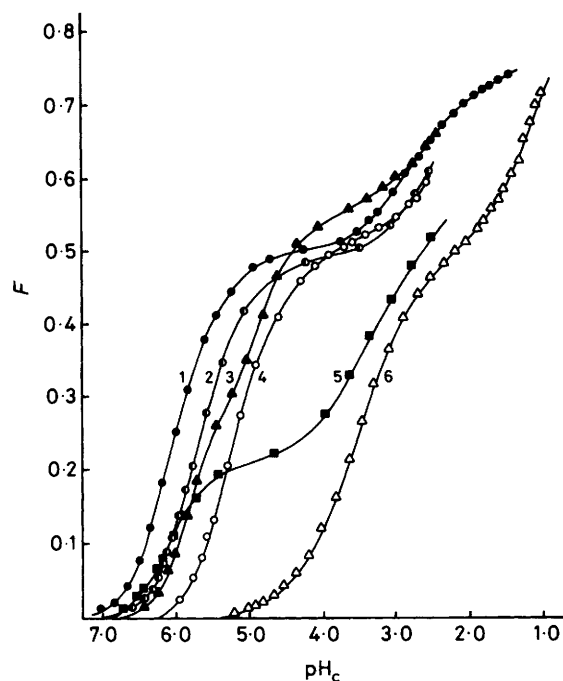
Figure 1. Function F versus pH_c for some representative potentiometric titrations. Concentrations: 1, $B = C = 0.05$; 2, $B = C = 0.01$; 3, $B = 0.01$, $C = 0.005$; 4, $B = C = 0.001$; 5, $B = 0.01$, $C = 0.04$; 6, $B = 0$, $C = 0.02$ mol dm^{-3}
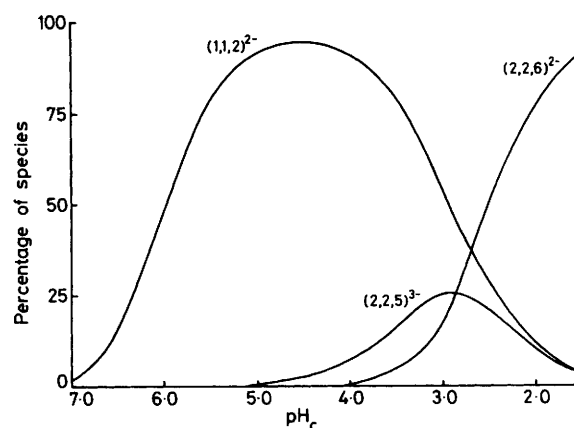
Figure 2. Concentration of complexes, expressed as a percentage of the total molybdenum(VI) concentration, as a function of pH_c for an equimolar solution of molybdate and oxalate (0.05 mol dm^{-3})

(4.1%). The $(2,2,4)^{4-}$ complex, however, was rejected (log β_{224} negative), while the relatively large standard deviation calculated for the $(1,2,4)^{2-}$ complex (18.5%) and the large value for the sum of squares (671 × 10^6) showed that this model was not correct. Subsequently, various other models were tried either by adding new species or by replacing species when the standard deviations of their equilibrium constants were too large (>33%). Several series of complexes with $p:q$ ratios of 1:1, 1:2, 2:1, and 2:2, each with different r values, were considered. Most of the species rejected in a particular model were introduced a second time in some other model, but were most often rejected again. The results obtained with some representative reaction models are summarised in Table 1. The reaction model finally selected as giving the best description of the experimental data comprised the following three complexes: $(1,1,2)^{2-}$, $(2,2,5)^{3-}$, and $(2,2,6)^{2-}$. Although the sum of squares (3.3 × 10^6) could still be decreased marginally (to 3.2 × 10^6) by

adding the $(1,1,3)^-$ complex to the model, its inclusion was not justified on the grounds of the large standard deviation of the equilibrium constant (51%).

Finally, as a check on the consistency of the data the formation constants of $HMo_7O_{24}{}^{5-}$ and $HC_2O_4{}^-$ were treated as unknowns together with those of the complexes. The values thus calculated for the constants (model G, Table 1) agree very well with those obtained previously, e.g. log $\beta_{011} = 3.52$ (this work) and log $\beta_{709} = 57.4$.[22]

The formation constant calculated for the $(1,1,2)^{2-}$ complex is in good agreement with the value reported by Johansen and Jøns[17] (log $\beta_{112} = 13.816$) for an ionic medium (0.15 mol dm^{-3} KNO$_3$). The $(1,1,2)^{2-}$ complex was the only complex identified by these authors, but their investigation was restricted to the pH range 4—7. The distribution curves in Figure 2 show that the other two species characterised in this investigation occur in very low concentrations at $pH_c > 4$. Also, the tendency for molybdenum(VI) to form polymeric species increases with increasing ionic strength.[25] It is, therefore, not surprising that these authors only found the $(1,1,2)^{2-}$ complex under the conditions of their investigation. The two dimeric complexes shown to exist in solution are all the more acceptable in view of the fact that the $(2,2,6)^{2-}$ complex has been isolated in the solid state as potassium and ammonium salts.[6]

The results of this investigation do not agree with those of Beltrán et al.[10] who postulated the three complexes $(1,2,2)^{4-}$, $(2,2,4)^{4-}$, and $(2,2,5)^{3-}$. A reaction model consisting of these

Table 1. Some reaction models and formation constants for the complexes

Complex	Reaction models (log $\beta_{pqr} \pm 3\sigma$)						
	A	B (Beltrán)	C	D	E ('Best')	F	G
$(1,1,2)^{2-}$	13.61 ± 0.05			13.62 ± 0.01	13.619 ± 0.004	13.619 ± 0.004	13.619 ± 0.003
$(1,1,3)^-$						15.15 ± 0.66	
$(1,2,2)^{4-}$		15.00 ± 0.15					
$(1,2,4)^{2-}$	23.46 ± 0.24			20.3 ± 1.2			
$(2,2,4)^{4-}$	Negative	28.72 ± 0.10	28.83 ± 0.08				
$(2,2,5)^{3-}$		32.03 ± 0.21	31.74 ± 0.22		31.20 ± 0.04	31.16 ± 0.07	31.21 ± 0.03
$(2,2,6)^{2-}$			34.14 ± 0.19	34.09 ± 0.05	34.08 ± 0.02	34.04 × 0.06	34.08 ± 0.02
$(0,1,1)^-$	a	a	a	a	a	a	3.51 ± 0.01
$(7,0,9)^{5-}$	a	a	a	a	a	a	57.3 ± 0.5
10^6 (e.s.s)[b]	671	506	379	35	3.3	3.2	3.1

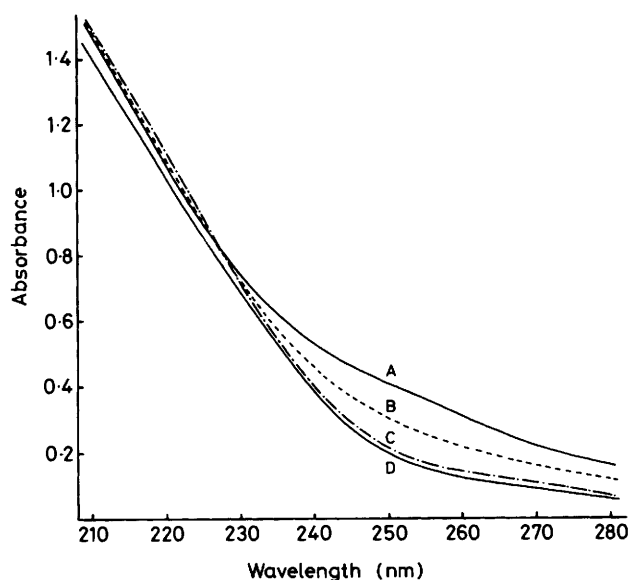[a] Values of constants were fixed at previously determined values (see text). [b] e.s.s. = Error square sum.

Figure 3. Change in absorption spectra with pH_c of a solution (0.005 mol dm^{-3} molybdate, 0.006 mol dm^{-3} oxalate, and 0.01 mol dm^{-3} hydrochloric acid) titrated with sodium hydroxide; pathlength 0.022 45 cm. A, pH_c 2.112; B, pH_c 2.558; C, pH_c 4.296; D, pH_c 5.076

Table 2. Values for equilibrium constants ($\log \beta_{pqr} \pm 3\sigma$) calculated from the spectrophotometric data for the best potentiometric model (E) and the model of Beltrán et al.[10] (B)

| | First experiment | | Second experiment |
Complex	E ('Best')	B (Beltrán)	E ('Best')
$(1,1,2)^{2-}$	13.62 ± 0.06		13.64 ± 0.01
$(1,2,2)^{4-}$		16.8 ± 0.8	
$(2,2,4)^{4-}$		30.3 ± 0.6	
$(2,2,5)^{3-}$	31.4 ± 0.1	32.5 ± 0.6	31.2 (fixed)
$(2,2,6)^{2-}$	34.3 ± 0.3		34.14 ± 0.04

complexes resulted in a much poorer fit (506×10^6) than that obtained with our best model (3.3×10^6). In fact most of the other models tried in this investigation gave a better fit than the model proposed by these authors. The formation constants reported for the complexes in their model, namely $\log \beta_{122} = 15.52$, $\log \beta_{224} = 16.5$, and $\log \beta_{225} = 14.6$, are completely different from the values computed from the data of the present investigation and also appear to be inconsistent; for example, the values of the formation constants for the $(2,2,4)^{4-}$ and $(2,2,5)^{3-}$ complexes imply that a hydrogen concentration of 79 mol dm^{-3} would be required to obtain equal concentrations of these two complexes in solution. It seems as if the spectrophotometric methods used by these authors lack the necessary sensitivity for the determination of the stoicheiometry and equilibrium constants of the species in such a complicated system, especially if the various side equilibria are neglected. Their isolation of the $(1,2,2)^{4-}$ and $(2,2,4)^{4-}$ complex ions from solution as the solid compounds $[Co(en)_3]_4[MoO_2(OH)_2$-$(C_2O_4)_2]_3 \cdot 8H_2O$ and $[Co(en)_3]_4[Mo_2O_5(OH)_2(C_2O_4)_2]_3 \cdot 6H_2O$ does not really prove that such complex ions exist in significant amounts in solution. In the spectrophotometric investigation described in the next section it will be seen that a sophisticated computer treatment of sufficient spectrophotometric data leads to the same conclusions as the potentiometric investigation.

Spectrophotometric Investigation.—The change in the

absorption spectrum with pH_c of a solution containing molybdate and oxalate is rather small and no prominent absorption peaks are observed (Figure 3). The spectrophotometric data are, therefore, not very suitable for stringent equilibrium analysis and model testing. However, by using a computer program such as SQUAD[26] which makes provision for the simultaneous treatment of absorption measurements at a number of wavelengths, it should be possible in principle to verify the validity of the reaction model deduced from the potentiometric investigation. If the model is correct it should at least result in a satisfactory fit between observed and calculated absorption values with equilibrium constants for the complexes of the same order of magnitude as those obtained by potentiometry.

The data from the two spectrophotometric titrations were treated separately. In the first experiment molybdate was titrated with oxalic acid and a spectrum of the solution was measured at 12 different pH_c values in the range 2.3—4.9. At pH_c 2.3 the solution contained an approximate ten-fold excess of oxalate over molybdate. Under the experimental conditions absorption by the species MoO_4^{2-}, $HMoO_4^-$, $C_2O_4^{2-}$, $HC_2O_4^-$, and $H_2C_2O_4$ in addition to that of the complexes had to be considered. The equilibrium constant and spectra for MoO_4^{2-} and $HMoO_4^-$ have earlier been reported for 1 mol dm^{-3} NaCl medium;[22,27] the spectra for the three oxalate species were calculated from absorbance measurements made in 1 mol dm^{-3} NaCl, using the potentiometrically determined equilibrium constants. These constants and spectra were all taken into account in the treatment of the data.

The computations, employing the program SQUAD and assuming that the reaction model deduced from the potentiometric investigation is correct, resulted in an excellent fit between experimental and calculated absorbances. The value obtained for $\log \beta_{112}$ was similar to that calculated from the potentiometric data (Table 2). The agreement between the spectrophotometric and potentiometric formation constants of the other two complexes may be regarded as quite satisfactory considering the small change in the absorption spectrum which occurs upon conversion of the $(1,1,2)^{2-}$ to the $(2,2,5)^{3-}$ and $(2,2,6)^{2-}$ complexes. The reaction model proposed by Beltrán et al.[10] not only resulted in a poorer fit, but the values for the formation constants of precisely the two complexes of which the formation is not substantiated by the results of the present investigation differed by more than 1.5 log units from the potentiometric values.

Another experiment was done at higher molybdate and oxalate concentrations using a shorter path length and taking absorbance measurements at every second wavelength in the range 210—300 nm. The main purpose of this experiment was to collect data to calculate the most accurate possible spectra for the complexes using the potentiometrically determined equilibrium constants. Only a very small excess of oxalate was used to minimise the correction needed for the absorption of uncomplexed oxalate species; an excess of oxalate, albeit small, is desirable to reduce the concentrations of uncomplexed molybdate species and their possible contribution to the measured absorption to negligible levels. Because spectra were recorded at only seven different pH_c values the data were not adequate for the calculation of as many as three formation constants. To check the consistency of the two sets of data the formation constant of the $(2,2,5)^{3-}$ complex, the minor species in the system, was therefore fixed at the potentiometric value in the treatment of the data. The values obtained for the formation constants of the other two complexes, namely $\log \beta_{112} = 13.64$ and $\log \beta_{226} = 34.14$, agreed very well with the potentiometrically determined values and the spectra calculated for the complexes from these data can, therefore, also be accepted as reliable. These spectra are shown in Figure 4. The spectrum of
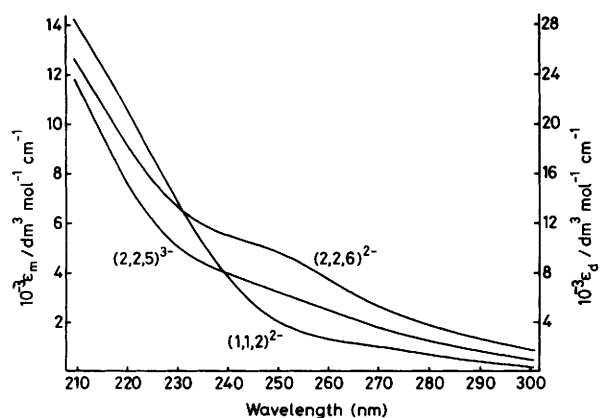
Figure 4. Calculated absorption spectra of complexes; ε_m and ε_d refer to mononuclear and dinuclear complexes respectively
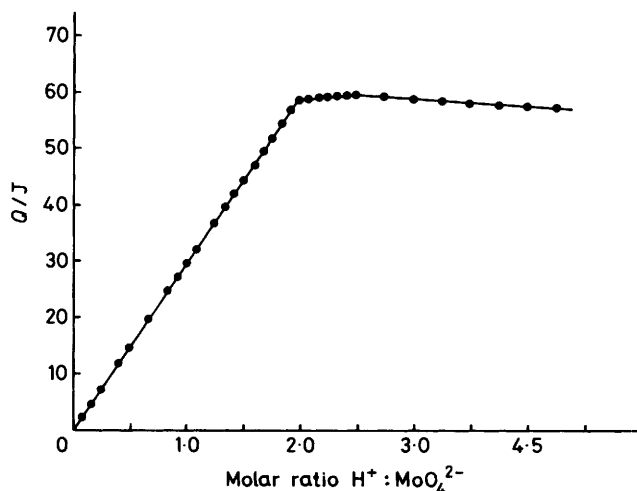

Figure 5. Measured heat, Q, as a function of the molar ratio of acid to molybdate (or oxalate) for a titration of an equimolar solution of molybdate and oxalate (1.00 mmol) with hydrochloric acid

Table 3. Formation constants and thermodynamic quantities for the molybdenum(VI) oxalate complexes in 1 mol dm^{-3} NaCl medium at 298 K

Complex	$(\log \beta_{pqr} \pm 3\sigma)$	$\Delta G^{\ominus}/$ kJ mol^{-1}	$\Delta H^{\ominus}/$ kJ mol^{-1}	$T\Delta S^{\ominus}/$ kJ mol^{-1}
$(1,1,2)^{2-}$	13.619 ± 0.004	-77.7	-59.5	18.2
$(2,2,5)^{3-}$	31.20 ± 0.04	-178.0	-123.0	55.0
$(2,2,6)^{2-}$	34.08 ± 0.02	-194.5	-117.0	77.5

the $(1,1,2)^{2-}$ complex resembles that of oxalate and its protonated products[19] and shows none of the characteristic absorption bands of monomeric molybdate species.[27] The spectrum of both the dinuclear complexes, however, has a shoulder at 240—250 nm which coincides with the absorption maximum of the dinuclear cationic molybdenum(VI) species.[28]

Calorimetric Investigation.—The results of an isothermal titration of a solution, containing 1 mmol of both molybdate and oxalate, with hydrochloric acid is shown in Figure 5 as a plot of the total amount of heat measured, Q, against molar ratio of acid to molybdate (or oxalate). The conditions chosen for the enthalpimetric titration were such that molybdate and oxalate side reactions could be ignored. The first part of the

curve is perfectly linear in accordance with the formation of only one species, i.e. the $(1,1,2)^{2-}$ complex (cf. Figure 2), and a sharp break is observed at the point where 2 mmol of acid have been added. Further addition of acid causes only a very small exothermic effect until 2.5 mmol of acid have been added. The slight break in the curve at this point corresponds to the stoicheiometry of the second complex, namely $(2,2,5)^{3-}$. The last part of the curve indicates that the protonation of the $(2,2,5)^{3-}$ complex is an endothermic process.

The enthalpy changes for complex formation were calculated from the measured heat (corrected for dilution effects) using equation (4), where n_{pqr} is the number of moles formed and

$$Q = \Sigma n_{pqr} \Delta H_{pqr}^{\ominus} \qquad (4)$$

$\Delta H_{pqr}^{\ominus}$ is the molar enthalpy change for the formation of a given complex at 25 °C in 1 mol dm^{-3} NaCl medium.

A value for $\Delta H_{112}^{\ominus}$ could be obtained from the slope of the first part of the straight line in Figure 5 where Q is directly proportional to the amount of $(1,1,2)^{2-}$ complex formed and to the amount of acid added. This value was then used in equation (4) to set up a series of linear equations with the two unknowns $\Delta H_{225}^{\ominus}$ and $\Delta H_{226}^{\ominus}$ from corresponding Q and n values for the rest of the titration curve. Values for n_{pqr} at each titration point were calculated from the concentrations of the species obtained by simultaneous solution (applying Newton's method[29]) of the three mass-balance equations 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 MoO_4^{2-}, $C_2O_4^{2-}$, and H^+ respectively. The set of simultaneous equations were then solved for $\Delta H_{225}^{\ominus}$ and $\Delta H_{226}^{\ominus}$ by the method of least squares.

The thermodynamic quantities for complexation are listed in Table 3. No values for enthalpy and entropy changes for molybdenum(VI) complex formation are listed in any of the standard reference sources. The thermodynamic parameters for the formation of the $(1,1,2)^{2-}$ complex, however, can be compared with those determined recently for the $(1,1,2)^{2-}$ complex of molybdate with citrate,[30] namely $\Delta G^{\ominus} = -86.1$, $\Delta H^{\ominus} = -60.2$, and $T\Delta S^{\ominus} = 25.9$ kJ mol^{-1}. The values, $\Delta H^{\ominus} = 6.0$ and $T\Delta S^{\ominus} = 22.5$ kJ mol^{-1}, for the protonation of the $(2,2,5)^{3-}$ oxalate complex are typical for the protonation of an anionic base for which $\Delta H^{\ominus}$ normally is a small positive or negative quantity, while $T\Delta S^{\ominus}$ has a value of $\sim(25 \pm 10)$ kJ mol^{-1} $(T = 298$ K).[31] These values also agree with those obtained for the protonation of the different citrate complexes of molybdenum(VI).[30]

The relatively large negative $\Delta H^{\ominus}$ values for the formation of the different complexes are not typical for complex formation, but can be interpreted in terms of additional bond energy arising from an increase in the co-ordination number of molybdenum(VI) from four to six. Comparable values for the enthalpy change for citrate complex formation have been obtained and also for the second protonation of molybdate which is associated with an expansion of co-ordination number from four to six.[32]

Conclusions

Three molybdenum(VI) oxalate complexes, namely $(1,1,2)^{2-}$, $(2,2,5)^{3-}$, and $(2,2,6)^{2-}$, have been shown to exist in solution in the pH$_c$ range 2—7 and have been characterised with respect to their u.v. absorption spectra, stability constants, and thermo-

dynamic parameters. The stoicheiometries of these complexes are consistent with the only complexes which have been structurally characterised by X-ray analysis,[5,6] *i.e.* the salts of complexes of the type $K_2[Mo_2O_5(C_2O_4)_2(H_2O)_2]$ and $K_2[MoO_3(C_2O_4)]\cdot H_2O$.

Acknowledgements

References

1 G. Spengler and J. Gansheimer, *Angew. Chem.*, 1957, **26**, 253.
2 P. C. H. Mitchell, *Chem. Soc. Rev.*, 1966, **20**, 103.
3 L. O. Atovymyan and G. B. Bokii, *J. Struct. Chem.*, 1963, **4**, 524.
4 B. Spivack and Z. Dori, *Coord. Chem. Rev.*, 1975, **17**, 99.
5 F. A. Cotton, S. M. Morehouse, and J. S. Wood, *Inorg. Chem.*, 1963, **3**, 1603.
6 B. F. Mentzen and H. Sauterau, *J. Photochem.*, 1981, **15**, 169.
7 J. Gopalakrishnan, B. Viswanathan, and V. Srinivasan, *J. Inorg. Nucl. Chem.*, 1970, **32**, 2565.
8 S. P. Goel and P. N. Mehrotra, *Thermochim. Acta*, 1983, **68**, 137.
9 S. P. Goel and P. N. Mehrotra, *Thermochim. Acta*, 1983, **70**, 201.
10 A. Beltrán, F. Caturla, A. Cervilla, and J. Beltrán, *J. Inorg. Nucl. Chem.*, 1981, **43**, 3277.
11 A. Beltrán-Porter and E. Martinez-Tamayo, *Thermochim. Acta*, 1984, **75**, 303.
12 A. Tchakirian and O. Vartapetian, *C.R. Acad. Sci. Paris*, 1952, **234**, 212.
13 R. A. Chalmers and A. G. Sinclair, *J. Inorg. Nucl. Chem.*, 1967, **29**, 2065.
14 D. A. Shishkor and B. Velcheva, *C.R. Acad. Bulg. Sci.*, 1964, **17**, 905.
15 M. Mikesova and M. Bartusek, *Collect. Czech. Chem. Commun.*, 1978, **43**, 1867.
16 K. Ya. Shapiro, Yu. N. Yurkevich, and V. V. Kulukova, *Chem. Abstr.*, 1968, **69**, 102644e.
17 E. S. Johansen and O. Jøns, *Talanta*, 1984, **31**, 743.
18 H. S. Rossotti, *Talanta*, 1974, **21**, 809.
19 J. J. Cruywagen and J. B. B. Heyns, *Talanta*, 1983, **30**, 197.
20 J. J. Christensen, H. D. Johnston, and R. M. Izatt, *Rev. Sci. Instrum.*, 1968, **39**, 1356.
21 J. J. Christensen, J. W. Gardner, D. J. Eatough, P. J. Watts, and R. M. Hart, *Rev. Sci. Instrum.*, 1973, **44**, 481.
22 J. J. Cruywagen, *Inorg. Chem.*, 1980, **19**, 552.
23 I. Grenthe, G. Gardhammar, and E. Rundcrantz, *Acta Chem. Scand.*, 1969, **23**, 93.
24 A. Sabatini, A. Vacca, and P. Gans, *Talanta*, 1974, **21**, 53.
25 K-H. Tytko, G. Baethe, and J. J. Cruywagen, *Inorg. Chem.*, 1985, **24**, 3132.
26 D. J. Leggett and W. A. E. McBryde, *Anal. Chem.*, 1975, **47**, 1065.
27 E. F. C. H. Rohwer and J. J. Cruywagen, *J. S. Afr. Chem. Inst.*, 1969, **22**, 198.
28 J. J. Cruywagen, J. B. B. Heyns, and E. F. C. H. Rohwer, *J. Inorg. Nucl. Chem.*, 1978, **40**, 53.
29 D. M. Hirst, 'Mathematics for Chemists,' MacMillan, London, 1976, p. 242.
30 J. J. Cruywagen and R. F. van de Water, *Polyhedron*, in the press.
31 J. J. Christensen, L. D. Hansen, and R. M. Izatt, 'Handbook of Proton Ionization Heats,' Wiley, London, 1976.
32 J. J. Cruywagen and E. F. C. H. Rohwer, *Inorg. Chem.*, 1975, **14**, 3136.