Complexation of Tungsten(VI) with Citrate

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Complex formation between tungstate and citrate (citric acid, H_4cit = 3-carboxy-3-hydroxypentane-1,5-dioic acid) has been investigated in the pH_c range 1.5–9.5 by potentiometric 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 side reactions of tungstate and citrate with hydrogen ions. The 'best' reaction model comprises eight complexes, representing four different tungstate–citrate stoichiometries. 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 $[(WO_4)_p(Hcit)_qH_r]^{(2p+3q-r)-}$, have the values $\log \beta_{111} = 10.21$, $\log \beta_{112} = 17.03$, $\log \beta_{113} = 21.67$, $\log \beta_{114} = 22.82$, $\log \beta_{224} = 34.89$, $\log \beta_{225} = 39.3$, $\log \beta_{126} = 34.51$ and $\log \beta_{214} = 31.7$. Enthalpy and entropy changes for the complexation reactions were calculated from the calorimetric data using the values of these formation constants. The enthalpy values for the major complexes are $\Delta H^\circ_{111} = -66$, $\Delta H^\circ_{112} = -67$ and $\Delta H^\circ_{113} = -78$ kJ mol^{-1}.

The formation in solution of either one or two complexes with a tungsten(VI) to citrate ratio of 1:1 has been reported by several authors (citric acid, H_4cit = 3-carboxy-3-hydroxypentane-1,5-dioic acid).[1–7] A complex with a 1:2 tungstate:citrate ratio has also been proposed by some of these investigators.[3,5,7] From the results of a spectrophotometric, polarimetric and NMR study Cervilla *et al.*[7] concluded that, in addition to a 1:1 and a 1:2 complex, two dimeric complexes with a tungstate:citrate ratio of 2:2 also exist in solution.

Despite agreement among investigators about the tungstate:citrate ratio of some complexes conclusions about the proton stoichiometry as well as the stability regions of most complexes are contradictory. For the 1:2 complex, for example, negative charges of 2− and 6−, respectively,[5,7] have been assigned.

To deduce the number and composition of the complexes from experimental data is particularly difficult because of the various side-equilibria that come into play. Protonation of both citrate and tungstate as well as condensation of tungstate, which can include slow reactions under certain conditions, must be taken into account. It has been shown in previous investigations that systems of this nature can be elucidated by equilibrium analyses through computer treatment of suitable potentiometric data.[8] A comprehensive potentiometric investigation was therefore carried out in which a number of complexes (including those with the tungstate:citrate ratios mentioned above) could be characterized in terms of stoichiometry and formation constants. Calorimetric data were also collected from which enthalpy and entropy changes for the formation of the major complexes could be calculated by using these formation constants.

Experimental

Reagents and Solutions.—Analytical grade chemicals (Merck p.a. and BDH Analar) were used and solutions were prepared with water obtained from a Millipore Milli-Q system. Sodium tungstate and sodium citrate were prepared from the recrystallized salts and the solutions standardized gravimetrically by evaporating known volumes to dryness and heating to constant weight at 160 °C. Hydrochloric acid was standardized indirectly against potassium hydrogenphthalate by titration with sodium hydroxide. Sodium chloride was purified as described previously.[9]

Potentiometric Titrations.—Mixtures of sodium tungstate and sodium citrate (50–90 cm^3) were titrated 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 tungstate and citrate, respectively, were as follows: 0.005, 0.025; 0.01, 0.01; 0.01, 0.02; 0.05, 0.075; 0.05, 0.10; 0.05, 0.20 and 0.10, 0.20. The titrations were done in duplicate and checked for consistency by comparing the plots of residuals produced by the computer program SUPERQUAD[10] used to treat the data. Some titrations were carried out manually to ensure that slow reactions were not overlooked. When citrate was in excess, stable potentials were obtained within seconds of addition of the titrant. In the case of an equimolar solution of tungstate and citrate of 0.05 mol dm^{-3}, for example, a drift in potential with time was observed which is typical of that which occurs in tungstate solutions acidified to $Z \gtrsim 1.2$ (Z = degree of protonation). Such titrations cannot be used to study the complexation equilibria. The highest equimolar concentration of tungstate and citrate used in the investigation, and which gave stable potentials in less than 1 min, was 0.01 mol dm^{-3}. A total of about 450 data points were collected and used in the computations.

The free hydrogen concentration, h, was determined by measuring the potential to ±0.2 mV using a Ross combination electrode (Orion) filled with 3.0 mol dm^{-3} KCl solution. Because of the relatively large volumes used in the experiments, contamination by small amounts of potassium ions during a titration could be ignored. The hydrogen-ion concentration was calculated from the measured potential, E, by use of equation (1). Values for E° and E_j (the liquid junction potential)

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

were determined from titrations of 1.0 mol dm^{-3} NaCl with HCl as described by Rossotti.[11] For brevity, $-\log h$ is denoted by pH_c.

Calorimetric Titrations.—An isothermal titration calorimeter, Tronac model 550, described elsewhere[12,13] was used for the enthalpy measurements. Solutions containing sodium

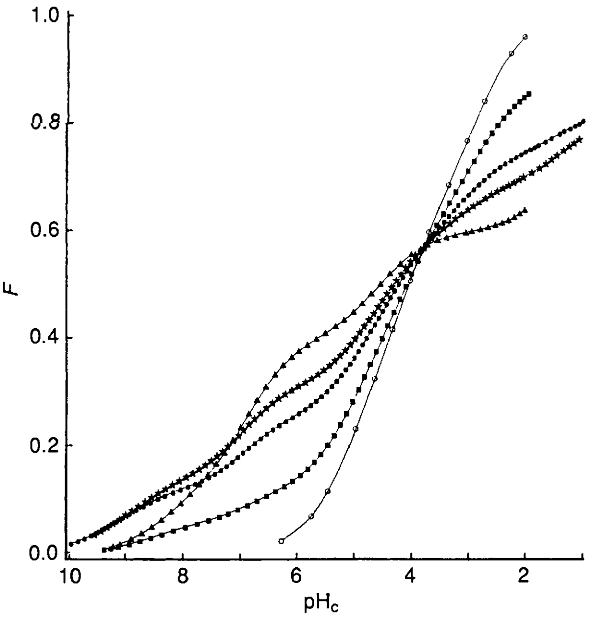

Fig. 1 Plots of function F *versus* pH_c for some representative potentiometric titrations. Initial concentrations (tungstate:citrate): (▲) 0.01:0.01, (★) 0.05:0.075, (●) 0.05:0.10, (■) 0.005:0.025 and (○) 0.00:0.02 mol dm^{-3}

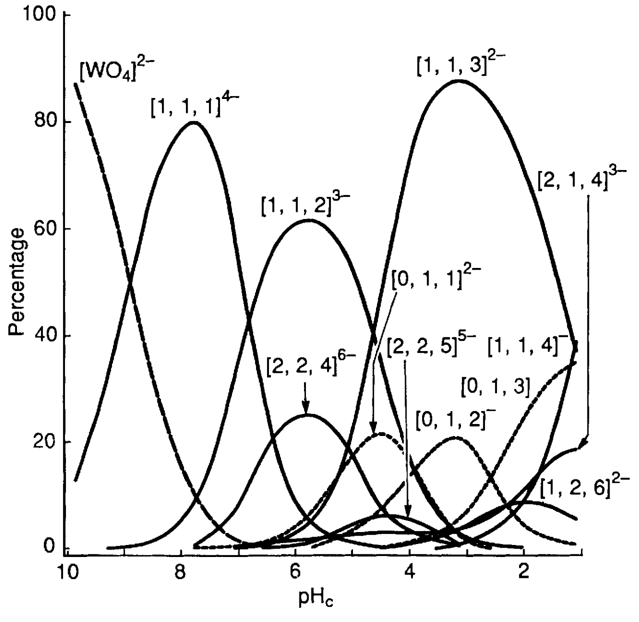

Fig. 2 Concentration of various species as a function of pH_c for the titration of a solution of 0.05 mol dm^{-3} tungstate and 0.075 mol dm^{-3} citrate. The concentrations are expressed as a percentage of the total tungsten(VI) (or total citrate for citrate species)

tungstate and sodium citrate (25.0 cm^3) were titrated with hydrochloric acid from a precision microburette (2.5 cm^3) and the data collected as described previously.[14] The initial concentrations of tungstate and citrate, respectively, were: 0.01, 0.01; 0.025, 0.03 and 0.05, 0.075 mol dm^{-3}. The titrations were carried out in duplicate and the pH_c range covered was 9.5–1.5. All solutions were made 1.0 mol dm^{-3} with respect to chloride ions by addition of recrystallized sodium chloride. To account for the endothermic heat effect when hydrochloric acid is titrated into sodium chloride the data were corrected by using results of previous blank titrations.[8,14]

Results and Discussion

Potentiometric Investigation.—The results of a number of potentiometric titrations are shown in Fig. 1 as normalized curves, *i.e.* as plots of F against pH_c. The function F represents the fraction of the total negative charge neutralized due to reaction with protons, equation (2) where H, B and C are the

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

analytical concentrations of hydrogen ions, tungstate and citrate, respectively. The reactions can be represented by the general equation (3) and for brevity species with overall

$$p[WO_4]^{2-} + q\mathrm{Hcit}^{3-} + r\mathrm{H}^+ \rightleftharpoons [(WO_4)_p(\mathrm{Hcit})_q\mathrm{H}_r]^{(2p+3q-r)-} \qquad (3)$$

formation constants β_{pqr} are denoted by the coefficients describing their stoichiometry, *i.e.* $[p,q,r]^{(2p+3q-r)-}$.

Inflections shown by the titration curves (Fig. 1) indicate the presence of relatively stable complexes at pH_c values 7.5, 5.5 and 3.0. For the titration of equimolar solutions of tungstate and citrate the inflections at $F \approx 0.4$ and 0.6 are consistent with the formation of complexes having a (p:q:r) stoichiometry of 1:1:2 and 1:1:3. It is seen that complex formation results in the uptake of protons at much higher pH_c than in the case of citrate alone. At low pH_c, on the other hand, protonation of the complexes is more difficult than that of citrate. Protonation of tungstate results in slow reactions at $Z \gtrsim 1.2$, but owing to the stability of the complexes these reactions are excluded when citrate is present. For equimolar solutions, however, the concentrations must be kept rather low if one wishes to avoid a drift in the pH_c (*cf.* Experimental section). To account for the presence of the tungstate polyanions $[W_6O_{20}(OH)_2]^{6-}$, $[W_7O_{24}]^{6-}$, $[HW_7O_{24}]^{5-}$ and $[H_2W_{12}O_{42}]^{10-}$ that occur at $Z < 1.2$, previously reported equilibrium constants for 1.0 mol dm^{-3} NaCl as medium[9] were used in the treatment of the potentiometric data. It was found, however, that due to the stability of the complexes only negligible amounts (<0.1%) of these tungstate species were present under the conditions of this investigation. It was therefore assumed that the formation of other tungstate polyanions at $Z > 1.2$ could also be neglected. Literature values for the protonation of citrate in 1.0 mol dm^{-3} NaCl medium[15] were used to make provision for the citrate side-equilibria in the calculations.

Model testing was done with the program SUPERQUAD.[10] In view of previous work, possible complexes with p:q ratios of 1:1, 1:2 and 2:2 were tried in the first computer runs; for each complex all possible r values were considered. It soon became apparent that the predominant species are mononuclear, namely $[1,1,1]^{4-}$, $[1,1,2]^{3-}$ and $[1,1,3]^{2-}$, but that several minor species must also be included to obtain a satisfactory description of the data. The reaction model arrived at, after having tested practically all possible complexes with p and q values up to four in various combinations, comprised eight complexes. In terms of the tungstate:citrate ratio three types of complexes occur, a series of four monomers $[1,1,1]^{4-}$, $[1,1,2]^{3-}$, $[1,1,3]^{2-}$, $[1,1,4]^{-}$, the two dimers $[2,2,4]^{6-}$ and $[2,2,5]^{5-}$, and two additional complexes, a monomer and a dimer for which $p \neq q$ namely $[1,2,6]^{2-}$ and $[2,1,4]^{3-}$. The values of the formation constants are listed in Table 1 and speciation curves are shown in Fig. 2.

The value of $s = 1.92$ (sample standard deviation[10]) based on estimated errors of 0.01 cm^3 in the volume and 0.002 in the pH_c, for seven different titrations, covering a very wide pH_c range, implies a very good fit. The relative standard error of the formation constant was greater than 4% for only two of the complexes, namely 9 and 19% for $[2,2,5]^{5-}$ and $[2,1,4]^{3-}$ respectively. Although the error of 19% is well below the limit of 33%, outside which a constant is usually regarded as being ill defined (and also automatically rejected by SUPERQUAD), one would have preferred an error closer to 10% before

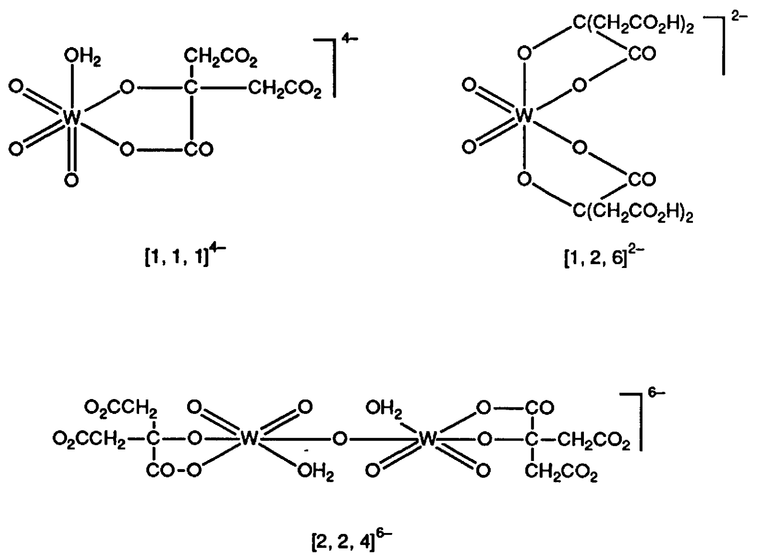

Fig. 3 Proposed structures for the complexes of tungsten(VI) with citrate

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

Complex	log β_{pqr} ± 3σ	$\Delta G°$	$\Delta H°$ ± 3σ	$T\Delta S°$
Tungsten(VI)				
[111]$^{4-}$	10.21 ± 0.01	−58.3	−66 ± 1	−7
[112]$^{3-}$	17.03 ± 0.01	−97.2	−67 ± 3	30
[113]$^{2-}$	21.67 ± 0.01	−123.7	−78 ± 1	46
[114]$^{-}$	22.82 ± 0.03	−130.2	−82 ± 6	48
[224]$^{6-}$	34.89 ± 0.06	−199.1	−190 ± 16	9
[225]$^{5-}$	39.33 ± 0.12	−224.5	−218 ± 33	6
[126]$^{2-}$	34.51 ± 0.03	−197.0	−134 ± 17	63
[214]$^{3-}$	31.68 ± 0.27	−180.8	−80 ± 30	101
Molybdenum(VI)[15]				
[111]$^{4-}$	8.25	−47.1	−49	−2
[112]$^{3-}$	15.08	−86.1	−60	26
[113]$^{2-}$	19.66	112.2	−67	45

accepting the complex in the model. The [2,1,4]$^{3-}$ complex could however not be 'proven' more conclusively because conditions favourable for its existence, *i.e.* an excess of tungstate, had to be avoided because of slow reactions and concomitant unstable potentials. A complex with similar stoichiometry has, however, been reported for the molybdate–citrate system.[15]

The mononuclear complexes [1,1,1]$^{4-}$, [1,1,2]$^{3-}$ and [1,1,3]$^{2-}$ which predominate in this system also occur in high percentages in the case of the molybdate–citrate system. A comparison of the formation constants of these complexes shows that the tungsten complex is in each case significantly more stable than the molybdenum complex, the difference in the values of the formation constants being 1.96, 1.95 and 2.01 log units. This difference in stability is caused mainly by the enthalpy change for complexation and is associated with the greater tendency of tungstate to increase its co-ordination from four to six (*cf.* next section). Also noteworthy are the almost identical values for the protonation constants of the tungsten and molybdenum complexes, namely 6.82 and 6.83 respectively for the protonation of the [1,1,1]$^{4-}$ complex, as well as 4.64 and 4.58 for the protonation of the [1,1,2]$^{3-}$ complex. This agreement between the values of the protonation constants of the tungsten and molybdenum complexes could indicate protonation of unco-ordinated carboxylate groups of citrate. It supports in part the structure proposed by Cervilla *et al.*[7] for the [1,1,1]$^{4-}$ tungsten citrate complex in which the two terminal carboxylate groups are not co-ordinated. Citrate therefore acts as a bidentate ligand, co-ordinating through the deprotonated oxygen of the central OH group and the oxygen of the vicinal carboxylate group, to form a five-membered ring with tungsten(VI). The other four co-ordination positions are occupied by two oxo (*cis*) and two hydroxo groups.[7] However, in view of the recently determined crystal structure of the molybdenum(VI) oxalate complex[16] $[(-)Co(en)_3][MoO_3(C_2O_4)(OH_2)]I{\cdot}2H_2O$ (en = ethylenediamine), a structure for the tungsten citrate complex with a *cis*-trioxo unit WO_3 and a co-ordinated H_2O (to complete the co-ordination sphere) is not unlikely (Fig. 3).

Also shown in Fig. 3 are possible structures for the [1,2,6]$^{2-}$ and [2,2,4]$^{6-}$ complexes. For these complexes having a *cis*-WO_2 unit it is assumed that the carboxyl oxygens are *trans* to these terminal oxygens similar to the situation in complexes of molybdenum(VI) with tartrate[17] $[NMe_4]_2[MoO_2(C_4H_4O_6)_2]{\cdot}EtOH{\cdot}1{\cdot}5H_2O$ and citrate[18,19] $[Mo_4O_{11}(Hcit)_2]^{4-}$. The results of this investigation are therefore in agreement with those of Cervilla *et al.*[7] as far as the composition of the [1,1,1]$^{4-}$ and [2,2,4]$^{6-}$ complexes is concerned. However the proton stoichiometry of the [1,2,6]$^{2-}$ and [2,2,5]$^{5-}$ species differs from that of the other two complexes proposed by these authors, *i.e.* the [1,2,3]$^{5-}$ and [2,2,7]$^{3-}$.

Enthalpimetric Investigations.—The results of two representative enthalpimetric titrations of a mixture of tungstate and citrate with hydrochloric acid are shown in Fig. 4. The total heat measured, corrected for dilution effects, Q, is plotted against the molar ratio of acid added to tungstate. It is seen that Q increases almost linearly with increase in the amount of acid added up to a molar ratio of 1:1 in accordance with the formation of the [1,1,1]$^{4-}$ complex. The enthalpy change associated with protonation reactions is usually a comparatively small positive or negative quantity. Consequently, a relatively small increase in the heat evolved is observed upon further addition of acid when successive protonation of this complex (and also of free citrate) takes place together with its conversion into the other minor species. The enthalpy changes for the formation of the various complexes were calculated from the calorimetric data by using equation (4) where n_{pqr} is the number of moles formed

$$Q = \Sigma\, n_{pqr} \Delta H^\circ_{pqr} \qquad (4)$$

and ΔH°_{pqr} is the molar enthalpy change for a given species $[p,q,r]$ at 25 °C in 1.0 mol dm^{-3} NaCl medium. The set of linear

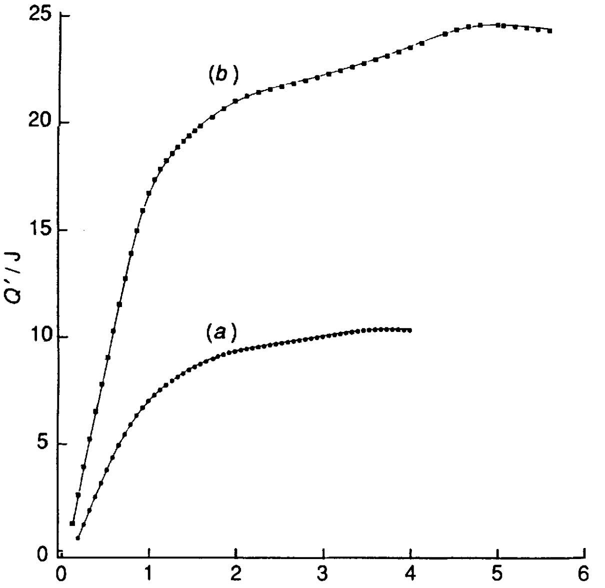

Fig. 4 Measured heat, Q', as a function of the molar ratio of acid to tungstate for a titration of (*a*) 0.025 mol dm^{-3} tungstate and 0.030 mol dm^{-3} citrate, and (*b*) 0.050 mol dm^{-3} tungstate and 0.075 mol dm^{-3} citrate with HCl (Q' = total heat minus heat generated during first two increments of acid)

equations obtained from corresponding Q and n_{pqr} values were solved for the unknown ΔH°_{pqr} parameters using a least-squares program.[20] The n_{pqr} values for each species were calculated from their concentrations (in a subroutine) by simultaneous solution of the three mass-balance equations (5)–(7) where b, c and h are

$$B = b + \Sigma p\beta_{pqr}b^pc^qh^r \quad (5)$$

$$C = c + \Sigma q\beta_{pqr}b^pc^qh^r \quad (6)$$

$$H = h + \Sigma r\beta_{pqr}b^pc^qh^r \quad (7)$$

the equilibrium concentrations of $[WO_4]^{2-}$, $Hcit^{3-}$ and H^+, respectively.

Previously determined ΔH° values for the protonation of citrate in 1 mol dm^{-3} NaCl were used in the treatment of the data to account for the small amount of heat involved in the protonation of free citrate.[15] Under the conditions chosen for the enthalpimetric titrations, protonation and condensation of free tungstate could be neglected. The thermodynamic quantities for the formation of the different complexes are listed in Table 1.

Because of the considerable overlap of equilibria and particularly those of the minor complexes (Fig. 2) the enthalpy changes for these minor complexes can be calculated only with limited accuracy. At worst the values could be regarded only as adjustable parameters in the calculation of the ΔH° values of the predominant complexes. However, the ΔH° and $T\Delta S^\circ$ values obtained for at least one of these minor complexes, $[1,1,4]^-$, fits reasonably well in the pattern set by the three major complexes $[1,1,1]^{4-}$, $[1,1,2]^{3-}$ and $[1,1,3]^{2-}$.

A feature of the thermodynamic quantities for complexation is the very favourable enthalpy change, which is ascribed to an increase in bond energy arising from an increase in the co-ordination number of tungsten from four to six. When the ΔH° value for formation of the $[1,1,1]^{4-}$ complex of tungsten(VI) and molybdenum(VI) is compared it is seen that the enthalpy change is about 17 kJ mol^{-1} more favourable for the tungsten complex and that it is mainly the effect of the enthalpy contribution which is responsible for the greater stability of this complex. A comparison of the thermodynamic quantities for the protonated complexes $[1,1,2]^{3-}$ and $[1,1,3]^{2-}$ leads to the same conclusion. This result then reflects the greater tendency of tungsten(VI) to increase its co-ordination number from four to six. This tendency is also seen when tetrahedral $[WO_4]^{2-}$ or $[MoO_4]^{2-}$ form polyanions in which all the tungsten(VI) and molybdenum(VI) atoms are octahedrally co-ordinated with respect to oxygen. The greater stability of $[W_7O_{24}]^{6-}$ compared to $[Mo_7O_{24}]^{6-}$, for example, has been shown to stem mainly from the enthalpy change,[9] the difference being 99 kJ mol^{-1} which amounts to about 14 kJ mol^{-1} for each tetrahedron that has been converted into an octahedron.

Conclusion

The results of this investigation show that the potentiometric data for tungsten(VI)–citrate complex formation is best interpreted in terms of the formation of eight complexes of which the three mononuclear complexes $[WO_3(cit)(OH_2)]^{4-}$, $[WO_3(Hcit)(OH_2)]^{3-}$ and $[WO_3(H_2cit)(OH_2)]^{2-}$ predominate at $pH_c > 2.0$. The formulation of the complexes is based on the structures proposed in Fig. 3, with the citrate anion, $C_6H_5O_7{}^{3-}$, denoted by $Hcit^{3-}$. It is assumed in acccordance with NMR evidence[7] that citrate co-ordinates through the central carboxylate oxygen and the adjacent hydroxyl oxygen to form a five-membered ring with tungsten. The other complexes are the singly charged monomer $[WO_2(H_2cit)(OH)(OH_2)]^-$, two dimers $[W_2O_5(cit)_2(OH_2)_2]^{6-}$ and $[W_2O_5(Hcit)(cit)(OH_2)_2]^{5-}$, and two complexes for which the tungsten:citrate ratio is 1:2 and 2:1 respectively, $[WO_2(H_2cit)_2]^{2-}$ and $[W_2O_6(Hcit)(OH_2)_2]^{3-}$. For the latter complex tridentate co-ordination of citrate to tungsten is assumed. Calorimetric data have been interpreted in terms of the formation of these complexes and values obtained for the formation constants were used to calculate enthalpy and entropy changes for the complexation reactions. These results show that the enthalpy change for the expansion of the co-ordination sphere from four to six is more favourable for tungsten than for molybdenum.

Acknowledgements

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