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Enthalpy of Oxidation-Reduction for the Ethylenediaminetetraacetatocobaltate(III/II) Couple Relative to the Hydrogen Ion Formation

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Oxidation of ethylenediaminetetraacetatocobaltate(II) with permanganate ion has been studied spectrophotometrically. The first step in the oxidation is the rapid formation of $[Co^{III}(edta)(H_2O)]^-$, followed by the ring closure reaction of the complex to $[Co^{III}(edta)]^-$. On the basis of the spectrophotometric result, the enthalpies of the reactions, $[Co^{II}(edta)]^{2-}+1/5\ MnO^-_4+8/5\ H^+\rightarrow[Co^{III}(edta)(H_2O)]^-+1/5\ Mn^{2+}+4/5\ H_2O$ and $[Co^{III}(edta)(H_2O)]^-\rightarrow[Co^{III}(edta)]^-+H_2O$, have been determined at 25 °C and at an ionic strength of 0.1 by a direct thermometric titration procedure. The enthalpy of the reaction, $[Co^{III}(edta)]^-+1/2\ H_2\rightleftharpoons[Co^{II}(edta)]^{2-}+H^+$, has been calculated by combining them with some other calorimetric data. The thermodynamic functions for formation of the $[Co^{III}(edta)]^-$ complex are estimated from the values so far reported. At 25 °C and at an ionic strength of 0.1 $\Delta G=-242$ kJ mol^{-1}, $\Delta H=-101$ kJ mol^{-1}, and $\Delta S=474$ J mol^{-1} K^{-1}.

The oxidation-reduction potential of a Co^{III}/Co^{II} system is reduced to a large extent in the presence of a complexing agent. It has been reported[1,2] that for the system in the presence of ethylenediaminetetraacetate(edta or L), the electrode reaction at a dropping mercury electrode is expressed by:

$$[Co^{III}(edta)]^- + e \rightleftharpoons [Co^{II}(edta)]^{2-},$$

its redox potential being reversible. The standard redox potential of the system has been determined by several authors[1–5] and furthermore, from information upon the stability constants of the Co(II)-edta complex and the standard redox potential of the $[Co(H_2O)_6]^{3+}/[Co(H_2O)_6]^{2+}$ couple,[6] the stability constant of the Co(III)–edta complex has been calculated. No thermodynamic function, however, has been reported for the $[Co^{III}(edta)]^-/[Co^{II}(edta)]^{2-}$ couple or the formation of the Co(III)–edta complex. Usually, the enthalpies of formation of Co(III) complexes can not be measured directly by a calorimetric method because they are substitution-inert. Cobalt(II) complexes are oxidized rapidly to form the corresponding Co(III) complexes. This is the case also for the edta complexes.[7,8] It is possible to measure heats of such rapid oxidation reactions by a calorimetric method and thus to obtain some information on the difference in enthalpies of the $[Co^{III}(edta)]^-/[Co^{II}(edta)]^{2-}$ couple, and thus, the enthalpy of formation of the Co(III)–edta complex. The present paper provides such information by determining the heat of oxidation of the Co(II)–edta complex with permanganate ion.

Experimental

Materials. The reagents used were Katayama super special grade potassium permanganate, Wako primary standard sodium oxalate, and Ventron iron(II) perchlorate. All other reagents used were of guaranteed reagent grade except for potassium nitrate and sodium perchlorate which were the same as described elsewhere,[9] while $K[Co^{III}(edta)]\cdot 2H_2O$[10] was prepared by the procedure described in the literature. The cobalt content of the complex was determined complexometrically[11] after thermal decomposition of the complex with perchloric and hydrochloric acids, the analytical value being 99.91% of the calculated value.

A stock solution of approximately 0.1 mol dm^{-3} in $Fe(ClO_4)_2$ and 0.2 mol dm^{-3} in $HClO_4$ was prepared and standardized against a 0.02 mol dm^{-3} solution of potassium permanganate, which was standardized against the primary standard sodium oxalate. Stock solutions of other metal ions were standardized by means of EDTA titrations.[11]

Measurements. All the measurements were made at 25.0 °C. The ionic strength of the solutions was maintained at 0.1 with potassium nitrate or sodium perchlorate. A Corning model 12 pH meter was used, the electrode system being standardized with the NBS standard buffer solutions. The pH values were converted to hydrogen ion concentrations by using an activity coefficient value of 0.782.[12]

Visible spectra were recorded on a Nippon Bunko UVIDEC-1 Spectrophotometer or a UNION High Sensitivity Spectrophotometer SM-401 with a thermostated cell compartment.

The titration calorimeter used was the same as described elsewhere.[13] The experimental procedure is described below with the treatment of thermograms. Once thermal equilibrium was established (temperature drift less than 2×10^{-4} °C for 10 min), a titrant (1—3 cm^3) was added to 130.0 cm^3 of a solution at a constant rate of 1.11 cm^3 min^{-1}, and the temperature change, ΔT, was recorded as a function of time, t. The ΔT *vs.* t curve recorded consisted of three parts: preperiod; titration period; afterperiod (for 10 min). Calibration was performed by using a standard heater set in the titration cell after each titration, the ΔT *vs.* t curve similarly consisting of three parts: preperiod; Joul heating period; afterperiod.

Upon heating by an electric heater at the rate of q' expressed in kJ s^{-1}, the ΔT *vs.* t curve is expressed by: $d(\Delta T)/dt=q'/C-\alpha(\Delta T)$ where α expressed in s^{-1} is Newton's cooling constant, which is considered to be constant during the heat measurements (for *ca.* 13 min), and C expressed in kJ K^{-1} is the heat capacity of the calorimeter vessel with its content of solution. The ΔT *vs.* t curve for the afterperiod is expressed by: $d(\Delta T)/dt=-\alpha(\Delta T)$. Solving two differential equations mentioned above, we obtained the following equation for the afterperiod: $\Delta T=q'(1-e^{-\alpha t_1})\times e^{-\alpha t}/\alpha C$, where t_1 is heating time. The values of α and C were refined by means of a least-squares method with a successive approximation. Reproducibilities of α and C obtained by analysis of the ΔT *vs.* t curve for 10 min of the afterperiod were within ±1.5% and ±0.2%, respectively.

The enthalpy of formation of the 1:1 Mn(II) acetato complex was estimated by titration of Mn(II) with edta in an acetate buffer solution. A 0.153 mol dm^{-3} solution of the tetrasodium salt of EDTA was added at the rate of

p' expressed in mol s^{-1} to solutions containing manganese(II) nitrate (1.12×10^{-2} mol dm^{-3}) and an acetate buffer (0.1 mol dm^{-3}) in the pH range from 3.7 to 5.0, the ionic strength being kept at 0.1 (=[AcOK]+[KNO$_3$]). EDTA was added in each run to be 2.89×10^{-3} mol dm^{-3} at the final concentration. The ΔT *vs.* t curve for the afterperiod was obtained in a similar manner as mentioned above: $\Delta T = -\Delta H_{\text{obsd}} \times p'(1-e^{-\alpha t_2})e^{-\alpha t}/\alpha C$, where t_2 was titration time, ΔH_{obsd} expressed in kJ mol^{-1} was the observed heat change, and the C value determined by the calibration was used. The values of ΔH_{obsd} and α were refined as for calibration. The treatment of ΔH_{obsd} will be described later in more detail. The values of ΔH_{obsd} and α for titration of Co(II) with edta in an acetate buffer solution and for titration of iron(II) perchlorate with permanganate ion in 0.1 mol dm^{-3} perchloric acid were also determined by the same method.

The heat of oxidation of the Co(II)–edta complex with permanganate ion was measured on adding freshly prepared potassium permanganate solution (0.02 mol dm^{-3}) at the rate of p' (mol s^{-1}) to solutions containing edta (2.5×10^{-3} mol dm^{-3}) and Co(II) nitrate in a 1:1.1 ratio and an acetate buffer (0.1 mol dm^{-3}) in the pH range from 3.6 to 5.8, the ionic strength being kept at 0.1 (=[AcOK]+[KNO$_3$]). Potassium permanganate was added in each run to give a 7:1 mole ratio of edta to $MnO^-{}_4$. The observed heat change results from dilution(ΔH_D), rapid oxidation(ΔH^c_{ox}), and slow ring closure reaction(ΔH_{el}) taking place in a Dewar vessel (see below about the definition in Eqs. 1, 2, and 9). The ΔT *vs.* t curve for the titration period is expressed by: $d(\Delta T)/dt = (q'_{ox}+q'_{el})/C - \alpha(\Delta T)$ where $q'_{ox} = -(\Delta H_D + \Delta H^c_{ox})\times p'$, $q'_{el} = -\Delta H_{el}\times d\{D[Co^{III}(edta)^-]\}/dt$, and $D[Co^{III}(edta)^-]$ is the change in moles of $[Co^{III}(edta)]^-$ formed. $D[Co^{III}(edta)^-]$ was calculated from a titration speed, p', and $d[Co^{III}(edta)^-]/dt = k[Co^{III}(edta)(H_2O)^-]$ in which the rate constant of k had been determined spectrophotometrically. The ΔT *vs.* t curve for the afterperiod is expressed by: $d(\Delta T)/dt = q'_{el}/C - \alpha(\Delta T)$. The differential equations were solved by the same treatment as described elsewhere.[14] Consequently, the ΔT *vs.* t curve for the afterperiod is expressed in a simple form: $\Delta T = -\Delta H_{mes}\times f(t) - \Delta H_{el}\times g(t)$, where $\Delta H_{mes} = \Delta H_D + \Delta H^c_{ox}$ and both $f(t)$ and $g(t)$ are a function of time. The values of ΔH_{mes} and ΔH_{el} were refined by means of a least-squares method. The values of C and α determined by calibration were used in the calculation of $f(t)$ and $g(t)$. The effective enthalpy of the oxidation, ΔH^c_{ox}, was obtained by subtracting ΔH_D from ΔH_{mes}.

Results

Oxidation of Co(II)–edta Complex with Permanganate Ion. Equilibrium data[15–17] so far reported indicate that the oxidation of the Co(II)–edta complex with permanganate ion or manganese dioxide in an acetate buffer solution produces the Co(III)–edta complex and Mn(II) ion as the final products. In the present reaction systems the following equilibrium is anticipated:

$$[Co^{II}(edta)]^{2-} + [Mn^{III}(edta)(H_2O)]^- \rightleftharpoons [Co^{III}(edta)]^- + Mn^{2+} + edta.$$

Judging from the equilibrium constant obtained for the reaction, the Mn(III)–edta complexes could be excluded under our experimental conditions. It is well known, however, that permanganate ion is powerful enough to oxidize EDTA molecules directly. For example, the absorbance at 527 nm of permanganate ion (0.3 mol cm^{-3}) was reduced to 70% of its initial value after 1 h at 25 °C and pH 4.5 in the presence of an excess EDTA (1.0 mol cm^{-3}). The decrease in absorbance, however, was little affected by the further addition of Zn(II) or Ni(II) to excess (3.0 mol cm^{-3}), where the absorbance decreased by less than 1.5% after 1 h. It is apparent that the addition of Zn(II) and Ni(II) prevent the oxidation of EDTA by forming edta complexes. The Co(III)–edta complexes were formed immediately when the reactants were mixed and thus, there would not occur the oxidation of, at least, free EDTA with permanganate ion under our experimental conditions.

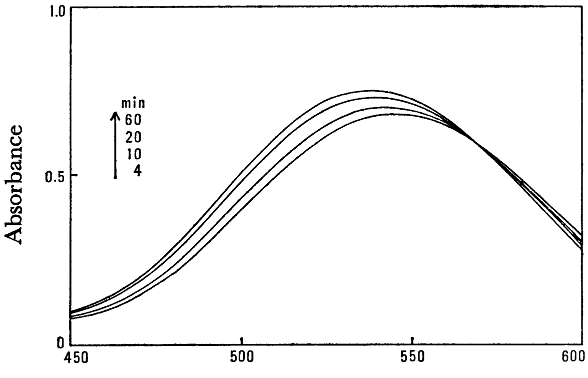

Fig. 1. The change of absorption spectrum with time after mixing Co(II)–edta complex with permanganate ion at pH 4.0.
$C_{Co(II)} = 2.7$ mol cm^{-3}; $C_{EDTA} = 2.5$ mol cm^{-3}; $C_{MnO_4} =$ 0.47 mol dm^{-3}.

The change in the absorption spectrum with time after mixing of the reactants is shown in Fig. 1. The wavenumbers of the absorption maxima at time zero and infinite time coincided with those of $[Co^{III}(edta)(H_2O)]^-$ ($\lambda_{max}=550$ nm)[8] and $[Co^{III}(edta)]^-$ ($\lambda_{max}=538$ nm),[18] respectively. The plot of the absorbance (538 nm) at infinite time against $5\times[MnO^-{}_4]/[Co(II)L]$ obtained under the condition as for Fig. 1 gave an inflection point at a ratio of 1.00 where minimum amounts of hydroxylamine required to reduce excess permanganate ions were added at the ratio more than 1.00. This indicates that little of the EDTA is lost and thus the following stoichiometry of the oxidation is held: $5Co(II)L + Mn(VII) \rightarrow 5Co(III)L + Mn(II)$. In addition, the molar absorptivity of the final product was derived to be 320 mol^{-1} dm^3 cm^{-1} by correcting for remaining reactants, the value being in agreement with that of $K[Co^{III}(edta)]\cdot 2H_2O$ prepared in this work ($\varepsilon_{max}=320$ mol^{-1} dm^3 cm^{-1}) and reported by Ogino, *et al.*[18] ($\varepsilon_{max}=321$ mol^{-1} dm^3 cm^{-1}). It is concluded that the oxidation of Co(II)–edta complex with permanganate ion rapidly proceeds to give $[Co^{III}(edta)(H_2O)]^-$ in quantitative yields and then the five-coordinate edta in the complex slowly becomes six-coordinate in the final product:

$$[Co^{II}(edta)]^{2-} + \tfrac{1}{5}MnO_4^- + \tfrac{1}{5}H^+ \longrightarrow [Co^{III}(edta)(H_2O)]^- + \tfrac{1}{5}Mn^{2+} + \tfrac{4}{5}H_2O \quad \Delta H_{ox}, \quad (1)$$

$$[\mathrm{Co^{III}(edta)(H_2O)}]^- \xrightarrow{k} [\mathrm{Co^{III}(edta)}]^- + \mathrm{H_2O} \quad \Delta H_{el}, \qquad (2)$$

where ΔH_{ox} is the enthalpy of Reaction 1 expressed in kJ mol^{-1} of [Co (edta)(H$_2$O)]$^-$, and ΔH_{el} the enthalpy of Reaction 2 expressed in kJ mol^{-1} of [Co^{III}(edta)]$^-$. Reaction 2 is first order in [Co^{III}(edta)(H$_2$O)]$^-$ concentration. Shimi and Higginson[19] determined the first-order rate constant, k, in the range of 0—15 °C. The rate constant of $1.6\times10^{-3}\,\mathrm{s^{-1}}$ estimated by extrapolation of the plot of k *vs.* $1/K$ to 25 °C was in good agreement with that determined in the present reaction systems ($1.61\times10^{-3}\,\mathrm{s^{-1}}$ at 25 °C).

Treatment of Observed Heat Change. Reaction 1 occurs accompanying the following side reactions:

$$[\mathrm{Co^{II}(edta)}]^{2-} + \mathrm{H^+} \rightleftharpoons [\mathrm{Co^{II}(Hedta)}]^- \quad K=10^{3.0},\ \Delta H_3=-8.0, \qquad (3)^{16)}$$

$$\mathrm{Mn^{2+}} + \mathrm{AcO^-} \rightleftharpoons [\mathrm{Mn(AcO)}]^+ \quad K=10^{0.5},\ \Delta H_4, \qquad (4)^{20)}$$

$$[\mathrm{Mn(AcO)}]^+ + \mathrm{AcO^-} \rightleftharpoons \mathrm{Mn(AcO)_2} \quad K=10^{0.9}, \qquad (5)^{20)}$$

$$\mathrm{Co^{2+}} + \mathrm{AcO^-} \rightleftharpoons [\mathrm{Co(AcO)}]^+ \quad K=10^{1.1},\ \Delta H_6, \qquad (6)^{20)}$$

$$[\mathrm{Co(A\text{ɔ}O)}]^+ + \mathrm{AcO^-} \rightleftharpoons \mathrm{Co(AcO)_2} \quad K=10^{0.4}, \qquad (7)^{20)}$$

$$\mathrm{H^+} + \mathrm{AcO^-} \rightleftharpoons \mathrm{AcOH} \quad K=10^{4.54},\ \Delta H_8=-0.17, \qquad (8)^{13)}$$

where K represents the equilibrium constant for the relevant reaction expressed in dm^3 mol^{-1} and ΔH the enthalpy expressed in kJ mol^{-1}. The values of K and ΔH reported in the relevant literature are used in this calculation, except for ΔH for Reactions 4—7 which are mentioned below. The measured heat, ΔH^c_{ox}, is given by:

$$\Delta H^c_{ox} = \Delta H_{ox} + \Delta H^c_3 + \Delta H^c_4 + \Delta H^c_6 + \Delta H^c_8, \qquad (9)$$

where

$$\Delta H^c_3 = \Delta H_3 \times D[\mathrm{Co^{II}(Hedta)^-}]/D[\mathrm{Co^{III}(edta)(H_2O)^-}], \qquad (10)$$

$$\Delta H^c_4 = \Delta H_4 \times \{D[\mathrm{Mn(AcO)^+}] + D[\mathrm{Mn(AcO)_2}]\}/D[\mathrm{Co^{III}(edta)(H_2O)^-}], \qquad (11)$$

$$\Delta H^c_6 = \Delta H_6 \times \{D[\mathrm{Co(AcO)^+}] + D[\mathrm{Co(AcO)_2}]\}/D[\mathrm{Co^{III}(edta)(H_2O)^-}], \qquad (12)$$

$$\Delta H^c_8 = \Delta H_8 \times D[\mathrm{AcOH}]/D[\mathrm{Co^{III}(edta)(H_2O)^-}], \qquad (13)$$

and $D[\ ]$ is the change in moles of species given in brackets for each titrant addition and is calculated from the stoichiometric relationships by using equilibrium constants for Reactions 3—8. Thus, the heat contribution due to Reaction 1 is calculated:

$$\Delta H_{ox} = \Delta H^c_{ox} - \Delta H^c_3 - \Delta H^c_4 - \Delta H^c_6 - \Delta H^c_8. \qquad (14)$$

A typical thermogram for titration of the Co(II)-edta complex with permanganate ion is shown in Fig. 2. In this case, ΔH^c_{ox} of -100.8 kJ mol^{-1} and ΔH_{el} of 4.4 kJ mol^{-1} were obtained. A plot of ΔH^c_{ox} *vs.* the final pH of the solution for each titration is shown in Fig. 3. The ΔH_{ox} values obtained over the pH range from 3.9 to 5.8 average -101.4 kJ mol^{-1} (solid line 1). Solid line 2 for ΔH^c_{ox} is the best fit line recalculated by using the average value of ΔH_{ox}. The calculated values of ΔH^c_6 were less than 0.03 kJ mol^{-1} over the pH range shown in Fig. 3. The broken line for ΔH^c_{ox}, which was measured at an ionic strength of 0.1 (=[AcONa]+[NaClO$_4$]), was lower than the solid line 2 by only *ca.* 0.5 kJ. In a solution of a low acetate concentration and an ionic strength, the effect of supporting electrolytes on ΔH^c_{ox} seems unimportant. The pH dependence of the ΔH_{el} values obtained at the same time could not be found in the pH region of 4.0 to 5.8 owing to the experimental errors. The ΔH_{el} value was determined to be 4.4±0.8 kJ mol^{-1}.

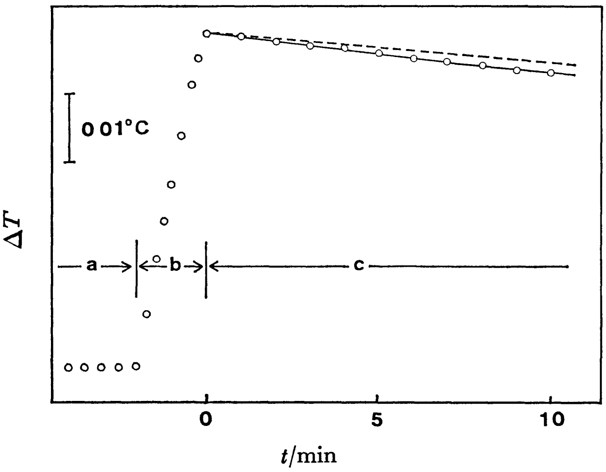

Fig. 2. Thermogram for the addition of permanganate ion to Co(II)-edta complex at pH 5.09. $C_{\mathrm{Co(II)}}=2.8$ mol cm^{-3}, $C_{\mathrm{EDTA}}=2.5$ mol cm^{-3}; $C_{\mathrm{MnO_4}}=0.38$ mol cm^{-3}. a: Preperiod, b: titration period, c: afterperiod. $\alpha=1.74\times10^{-4}\,\mathrm{s^{-1}}$; $k=1.61\times10^{-3}\,\mathrm{s^{-1}}$. Solid line is the best fit one calculated from the enthalpies ΔH_{mes} and ΔH_{el}. Broken line is the presumed curve calculated with $\Delta H_{el}=0$.

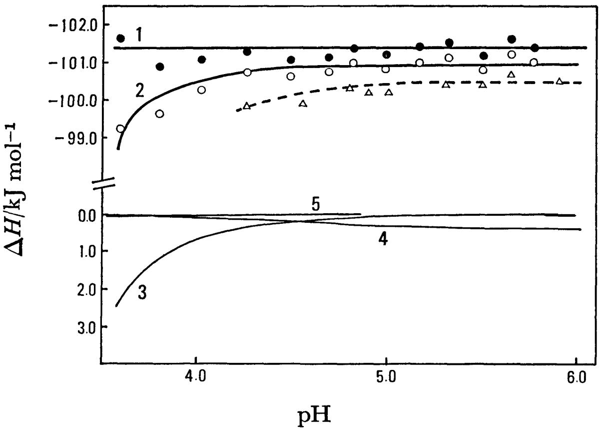

Fig. 3. ΔH^c_{ox} *vs.* the final pH of solution. Conditions as for Fig. 2.
○: ΔH^c_{ox} measured at $\mu=0.1$ (=[AcOK]+[KNO$_3$]), △: ΔH^c_{ox} measured at $\mu=0.1$ (=[AcONa]+[NaClO$_4$]), ●: ΔH_{ox} calculated according to Eq. 14. The solid lines represent: (1) the average value of ΔH_{ox}; (2) ΔH^c_{ox} recalculated with the average value of ΔH_{ox}; (3) ΔH^c_3; (4) ΔH^c_4; (5) ΔH^c_8.

The enthalpies of formation of the acetato complexes were mostly determined at an ionic strength of 1.0 or 3.0. As little knowledge of the enthalpy values determined in lower ionic media is available, the value for Mn(II) acetato complexes was estimated by titration of Mn(II) in 0.1 mol dm^{-3} acetate buffer solutions with the tetrasodium salt of EDTA. The observed heat, ΔH_{obsd}, refers to the process:

$$Mn^{2+\prime} + L(titrant) \longrightarrow Mn(II)L' \qquad \Delta H_{obsd}, \qquad (15)$$

where $[Mn^{2+\prime}] = [Mn^{2+}] + [Mn(AcO)^+] + [Mn(AcO)_2]$ and $[Mn(II)L'] = [Mn^{II}(edta)^{2-}] + [Mn^{II}(Hedta)^-]$. The process of Eq. 15 comprises that of dilution of 0.153 mol dm^{-3} Na_4edta (Eq. 16) and formation of $[Mn^{II}(edta)]^{2-}$ complex (Eq. 17):

$$L(titrant) \longrightarrow edta \qquad \Delta H_D, \qquad (16)$$

$$Mn^{2+} + edta \rightleftharpoons [Mn^{II}(edta)]^{2-} \qquad \Delta H_{17}, \qquad (17)$$

in which Reaction 17 accompanies Reactions 4, 5, and 8 and furthermore the following side reaction:

$$[Mn^{II}(edta)]^{2-} + H^+ \rightleftharpoons [Mn^{II}(Hedta)]^- \quad K = 10^{3.1},\ \Delta H = -5.0, \qquad (18)^{16)}$$

where K and ΔH are defined as for Eqs. 3—8. In such solutions containing 0.1 mol dm^{-3} acetate buffer, the 1:2 acetato complex is not present in amounts sufficient enough to permit the determination of the enthalpy value. Thus, the heat contribution due to stepwise formation of the 1:2 acetato complex is neglected as for Eq. 9 (*cf.* Eq. 11). The observed heat is corrected for ΔH_D, the value of which has been determined by the same method as described elsewhere.[9] Then, the following equations are obtained:

$$\begin{aligned}\Delta H_{cor} &= \Delta H_{obsd} - \Delta H_D \\ &= \Delta H_{17} + \Delta H^c_4 + \Delta H^c_{18} + \Delta H^c_8 \\ &= \Delta H_{17} + \Delta H_4 \times \{D[Mn(AcO)^+] \\ &\quad + D[Mn(AcO)_2]\}/D[Mn(II)L'] + \Delta H^c_{18} + \Delta H^c_8, \end{aligned} \qquad (19)$$

where

$$\begin{aligned}\Delta H^c_4 &= \Delta H_4 \times \{D[Mn(AcO)^+] \\ &\quad + D[Mn(AcO)_2]\}/D[Mn(II)L'], \\ \Delta H^c_{18} &= \Delta H_{18} \times D[Mn^{II}(Hedta)^-]/D[Mn(II)L'], \\ \Delta H^c_8 &= \Delta H_8 \times D[AcOH]/D[Mn(II)L'], \\ D[Mn(II)L'] &= D[Mn^{II}(edta)^{2-}] + D[Mn^{II}(Hedta)^-].\end{aligned}$$

A least-sequares analysis is performed to provide ΔH_{17} and ΔH_4 in Eq. 19. A plot of ΔH_{cor} *vs.* the final pH of the solution for each titration is shown in Fig. 4. The best fit line was calculated by using the values, $\Delta H_{17} = -18.7$ kJ mol^{-1} and $\Delta H_4 = 6.3$ kJ mol^{-1}. The broken lines are for each ΔH on the right hand side of Eq. 19. The ΔH^c_8 values were less than 0.05 kJ mol^{-1} over the pH range shown in Fig. 4. The enthalpy of formation of the 1:1 Co(II) acetate complex was estimated to be 2.3±0.3 kJ mol^{-1} by the same method as above, from which the ΔH^c_6 values in Eq. 9 were calculated to be less than 0.07 kJ mol^{-1}.

The heat of oxidation of iron(II) ion with permanganate ion was measured in 0.1 mol dm^{-3} $HClO_4$. For the reaction

$$Fe^{2+} + \tfrac{1}{5}MnO_4^- + \tfrac{8}{5}H^+ \longrightarrow Fe^{3+} + \tfrac{1}{5}Mn^{2+} + \tfrac{4}{5}H_2O \quad \Delta H_{20}, \qquad (20)$$

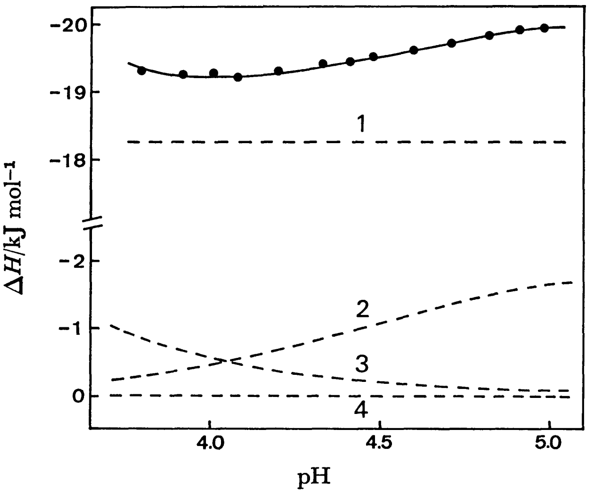

Fig. 4. ΔH_{cor} *vs.* the final pH of solution. $C_{Mn(II)} = 11.0$ mol cm^{-3}; $C_{EDTA} = 2.9$ mol cm^{-3}. ●: ΔH_{cor} measured at $\mu = 0.1$ $(= [AcOK] + [KNO_3])$. Solid line is the best fit one calculated from the enthalpies ΔH_{17} and ΔH_4. The broken lines represent: (1) ΔH_{17}; (2) ΔH^c_4; (3) ΔH^c_{18}; (4) ΔH^c_8.

we determined $\Delta H_{20} = -123.9 \pm 0.7$ kJ mol^{-1} of Fe^{3+}, in which the following side reaction was considered:

$$Fe^{3+} + H_2O \rightleftharpoons FeOH^{2+} + H^+ \quad K = 10^{-2.50},\ \Delta H = 42.3. \qquad (21)^{13)}$$

Discussion

A solution containing $[Co^{II}(edta)]^{2-}$ and $[Co^{III}(edta)]^-$ exhibits a reversible potential at a dropping mercury electrode.[2] It is possible to measure the standard redox potential, E°, with the solutions containing varied concentrations of $[Co^{II}(edta)]^{2-}$ and $[Co^{III}(edta)]^-$ complexes. For the reaction

$$[Co^{III}(edta)]^- + \tfrac{1}{2}H_2 \rightleftharpoons [Co^{II}(edta)]^{2-} + H^+, \qquad (22)$$

the ΔG value is calculated from E° value determined by several authors[1–5] by use of the relation, $\Delta G = nFE^\circ$. On the other hand, the products formed by oxidation of the Co(II)–edta complexes with a variety of oxidants are not always the same as that by the electrode oxidation; the Co(II)–edta complexes are oxidized to form Co(III)–edta complexes containing five- or six-coordinate edta, or their mixture.[7,8] It was found that the oxidation by permanganate ion produced $[Co^{III}(edta)(H_2O)]^-$ under our experimental conditions, followed by the ring closure reaction of the complex to $[Co^{III}(edta)]^-$. For the reaction

$$[Co^{II}(edta)]^{2-} + \tfrac{1}{5}MnO_4^- + \tfrac{8}{5}H^+ \longrightarrow [Co^{III}(edta)]^- + \tfrac{1}{5}Mn^{2+} + \tfrac{4}{5}H_2O, \qquad (23)$$

at an ionic strength of 0.1, therefore, we obtained $\Delta H = -97.0$ kJ mol^{-1} from the sum of ΔH values for Reactions 1 and 2. In order to convert a ΔH for the reaction to one for Reaction 22, the ΔH and ΔH°_f values mentioned below were adopted. For the reaction

$$Fe^{2+} + \tfrac{1}{2}H_2O_2(aq) + H^+ \longrightarrow Fe^{3+} + H_2O, \qquad (24)$$

in 0.1 mol dm^{-3} $HClO_4$, Irving, *et al.*[21] obtained

$\Delta H = -146.0 \pm 0.8$ kJ mol^{-1}. Correcting it for the side reaction 21, we obtained $\Delta H = -147.3$ kJ mol^{-1}. Combination of this value with the standard enthalpies of formation of $H_2O(l)$ and $H_2O_2(aq)$ listed in N. B. S. Technical Notes[22] leads to $\Delta H = -43.0$ kJ mol^{-1} for the following reaction:

$$Fe^{3+} + \tfrac{1}{2}H_2(g) \rightleftharpoons Fe^{2+} + H^+. \qquad (27)$$

A ΔH° of -42 kJ mol^{-1} or -40.6 kJ mol^{-1} for the reaction was recommended without consideration of ionic strength by Hepler, *et al.*[23] and in N. B. S. Technical Notes,[22] respectively. It is still difficult to estimate the effect of ionic strength on ΔH for the reaction from data so far reported. A ΔH of -69.9 kJ mol^{-1} for Reaction 22 was obtained from ΔH for Reactions 20, 23, and 27. ΔG for Reaction 22 was calculated to be -37.1 kJ mol^{-1} by use of $E^\circ = 0.384$ V[1] (*vs.* NHE) measured at an ionic strength of 0.1 and then, the ΔS value was calculated to be -110 J mol^{-1} K^{-1}.

Reaction 22 comprises the following reactions:

$$Co^{3+} + \tfrac{1}{2}H_2 \rightleftharpoons Co^{2+} + H^+, \qquad (28)$$

$$Co^{2+} + \text{edta} \rightleftharpoons$$
$$[Co^{II}(\text{edta})]^{2-} \quad K = 10^{16.23},\ \Delta H = -17.6, \qquad (29)^{16)}$$

$$Co^{3+} + \text{edta} \rightleftharpoons [Co^{III}(\text{edta})]^-. \qquad (30)$$

Thus, it is possible to calculate the ΔH value for Reaction 30 by use of the ΔH values for Reactions 22, 28, and 29. But the exact values of ΔG and ΔH at low ionic strengths for Reaction 28 have not been yet estimated from the appropriate data. For the reaction

$$Co^{3+} + Fe^{2+} \longrightarrow Co^{2+} + Fe^{3+}, \qquad (31)$$

in 4 mol dm^{-3} $HClO_4$ at 15 °C, Johnson and Sharpe[24] determined $\Delta H = -110$ kJ mol^{-1} by a direct calorimetric measurement. They combined it with the estimated entropy change (13 J mol^{-1} K^{-1}) to obtain ΔG of -114 kJ mol^{-1} at 15 °C. Neglecting a temperature dependence of ΔH, we obtained ΔG of -114 kJ mol^{-1} ($\Delta E = E^\circ_{28} - E^\circ_{27} = 1.18$ V) at 25 °C by the same manner. Combining it with the formal Fe^{3+}/Fe^{2+} potential of 0.749 V[25] at 25 °C and at an ionic strength of 0.1, we obtained the formal Co^{3+}/Co^{2+} potential of 1.93 V (*vs.* NHE) and thus ΔG of -186 kJ mol^{-1} for Reaction 28. Similarly the variation of ΔH for two half cell reactions involved in Eq. 31 with ionic strengths would adequately compensate each other because of the close similarity in size and charge of the pair of ions. Thus, the ΔH value for Reaction 28 was obtained to be -153 kJ mol^{-1} by summation of the ΔH values for Reactions 27 and 31 and thus the ΔS value was calculated to be -111 J mol^{-1} K^{-1}. The entropy change accompanying Reaction 28 can be represented by:

$$\Delta S^\circ = \overline{S}^\circ_{Co^{2+}} + \overline{S}^\circ_{H^+} - \overline{S}^\circ_{Co^{3+}} - \tfrac{1}{2}\overline{S}^\circ_{H_2}, \qquad (32)$$

where $\overline{S}^\circ$ is the standard partial molal entropy of the species involved. ΔS° is approximate to ΔS and thus the $\overline{S}^\circ_{Co^{3+}}$ values is calculated to be -290 J mol^{-1} K^{-1} by combining ΔS with $\overline{S}^\circ_{Co^{2+}}$ and $\overline{S}^\circ_{H_2}$ listed in N. B. S. Technical Notes.[22] The formal Co^{3+}/Co^{2+} potential of 1.84 V (*vs.* NHE) was determined at 25 °C and 3 mol dm^{-3} HNO_3 by use of a gold electrode,[26] the value being commonly used as that at ionic strengths of 0.1—0.2 in calculations[1–5] of the formation constants of the Co(III)–aminopolycarboxylate complexes. Combination of the ΔG value calculated from the potential with the ΔH value selected for Reaction 28 leads to the $\overline{S}^\circ_{Co^{3+}}$ value of -260 J mol^{-1} K^{-1}. This value seems to be too low compared with the $\overline{S}^\circ$ values of Fe^{3+} ion, which is similar to the size, mass, and charge of Co^{3+} ion, currently accepted: -316 (N. B. S.),[22] -293 (Latimer),[27] and -280 J mol^{-1} K^{-1} (Hepler).[23] From the ΔG and ΔS values determined for Reaction 22 and selected for Reactions 28 and 29, we obtained ΔG of -242 kJ mol^{-1} and ΔH of -101 kJ mol^{-1} as the most probable values for Reaction 30. Thus, the ΔS value was calculated to be 474 J mol^{-1} K^{-1}.

It was reported by Staveley[28] that a plot of ΔS for the formation of the metal(III)–edta complexes against the reciprocal of the ionic radius, r, of metal ion gave a curve with upward curvature. The ΔS values selected by Martell and Smith[16] were replotted against $1/r$, taken from Ahren's table,[29] the value for the Co(III) complex being situated upward the curvature only by *ca.* 30 J mol^{-1} K^{-1}. On the other hand, the ΔH value for the Co(III)–edta complex is much more exothermic than that for the metal(III)–edta complexes so far reported; ΔH of -30.1 kJ mol^{-1} for the In(III)–edta complex has been reported as the most exothermic ΔH value. It is reasonable to conclude, therefore, that the formation of the Co(III)–edta complex exhibits a normal entropy change, which is explained by the size and charge of the ion, together with that of other metal(III) complexes, whereas the enthalpy change for formation of the Co(III)–edta complex causes the complex to be the most stable of the metal(III)–edta complexes.

In a previous paper[13] ΔH of -11.5 kJ mol^{-1} and ΔS of 440 J mol^{-1} K^{-1} were reported for the formation of the Fe(III)–edta complex. The ΔS value for the Co(III) complex is somewhat higher than that for the Fe(III) complex. This would arise from the difference in the number of water molecules displaced from the coordination sphere of the aqua ion by the complex formation; Co^{3+} ion forms hexacoordinate complex, $[Co^{III}(\text{edta})]^-$, with edta, while Fe^{3+} ion forms heptacoordinate complex, $[Fe^{III}(\text{edta})(H_2O)]^-$.[30,31] The favorable enthalpy effect for formation of the Co(III)–edta complex is compatible with the facts that in the solid state the Co(III)–N bond-length (1.93 Å)[32] of the hexacoordinate Co(III)–edta complex is much shorter than the Fe(III)–N bond-length (2.32 Å)[33] of the heptacoordinate Fe(III)–edta complex and that Co^{3+} forms a low-spin complex with edta,[34] while Fe^{3+} forms a high-spin complex in weakly acid solution.[35] The redox potentials of the Co^{III}/Co^{II} and Fe^{III}/Fe^{II} systems are reduced from 1.93 V to 0.38 V and from 0.749 V to 0.12 V,[36] respectively, in the presence of EDTA. The larger decrease in the potential of the Co^{III}/Co^{II} system is caused by the enthalpy effect for formation of the Co(III)–edta complex because the thermodynamic functions for formation of the Co(II)– and Fe(II)–edta complexes are similar to each other.[16)]

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