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THE EQUILIBRIUM AND KINETIC STUDIES OF THE REACTION OF ETHYLENEDIAMINETETRA-ACETATOAQUACHROMATE(III) ION WITH ACETATE ION

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The equilibrium constant, K, and the rate constants for the reaction,

$$\mathrm{Credta(H_2O)^-} + \mathrm{OAc^-} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \mathrm{Cr(OAc)edta^{2-}} + \mathrm{H_2O}$$

were determined spectrophotometrically to be 0.61 M^{-1} for K, 8.7 M^{-1} s^{-1} for k_f and 14 s^{-1} for k_b at ionic strength 1.0 ($NaClO_4$) and 25 °C.

Schwarzenbach and Biedermann showed that chromium(III)-EDTA complex contains one water molecule in the sixth coordination site$^{1)}$, where EDTA denotes ethylenediaminetetraacetate. However, no example has been reported of the mixed ligand complex of chromium(III)-EDTA in which the sixth coordination site is occupied by a ligand other than water molecule. Thorneley et al. attempted to prepare $\mathrm{Cr(X)Hedta^-}$ ($X = Cl^-$ and Br^-), but obtained the complexes of the composition, $\mathrm{Cr(X)_2H_3edta(H_2O)}$, in which EDTA functioned as a terdentate$^{2)}$.

It was found in this work that, when the acetate buffer solution was added to the solution of $\mathrm{Credta(H_2O)^-}$, the visible absorption maxima shifted to longer wavelengths spontaneously. When the concentration of the acetate ion was varied, isosbestic points were observed on the absorption spectra. Figure 1 shows such a spectral change. This phenomenon could be interpreted reasonably by considering a rapid establishment of the following equilibrium:

$$\mathrm{Credta(H_2O)^-} + \mathrm{OAc^-} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \mathrm{Cr(OAc)edta^{2-}} + \mathrm{H_2O} \qquad (1)$$

This letter presents the spectrophotometric determination of the equilibrium constant, K, of the reaction (1);

$$K = \frac{[\mathrm{Cr(OAc)edta^{2-}}]}{[\mathrm{Credta(H_2O)^-}][\mathrm{OAc^-}]}$$

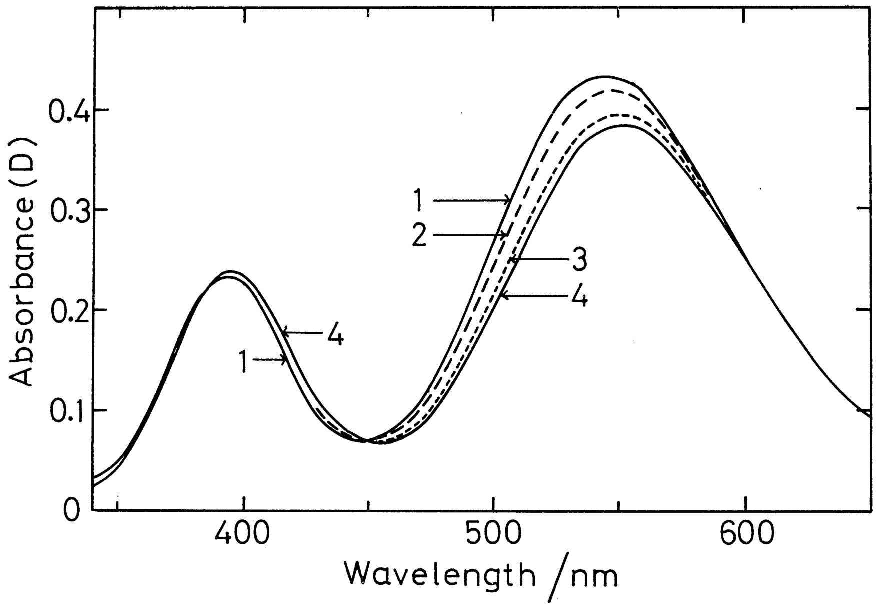

Fig. 1 Spectral change of chromium(III)-EDTA with the varied acetate ion concentrations. $[Cr(III)\text{-}EDTA]_{total}$ = 2.04 mM. $[OAc^-]$ = 0 (1), 0.20 (2), 0.60 (3) and 0.80 M (4)

and the rate constants given in Eq. (1).

All measurements were carried out at ionic strength 1.0 ($NaClO_4$) and 25.0 °C. The pH of the solutions was adjusted to be 4.5 with acetic acid-sodium acetate buffer solutions.

Determination of equilibrium constant The absorbance of chromium(III)-EDTA in an acetate buffer solution for unit cell length, D, is given by the equation,

$$D = \varepsilon_1[\mathrm{Credta(H_2O)^-}] + \varepsilon_2[\mathrm{Cr(OAc)edta^{2-}}] = (\varepsilon_1 + \varepsilon_2 K[\mathrm{OAc^-}])\frac{[\mathrm{Cr(III)}]_{total}}{1 + K[\mathrm{OAc^-}]} \qquad (2)$$

where ε_1 and ε_2 represent the molar extinction coefficients of $Credta(H_2O)^-$ and $Cr(OAc)edta^{2-}$, respectively. Equation (2) is rewritten as follows:

$$\frac{1}{\bar{\varepsilon} - \varepsilon_1} = \frac{1}{\varepsilon_2 - \varepsilon_1} + \frac{1}{\varepsilon_2 - \varepsilon_1} \times \frac{1}{K[\mathrm{OAc^-}]} \qquad (3)$$

where

$$\bar{\varepsilon} = \frac{D}{[\mathrm{Cr(III)}]_{total}}$$

Plots of $1/(\bar{\varepsilon} - \varepsilon_1)$ vs. $1/[OAc^-]$ gave linear relations as shown in Fig. 2. The equilibrium constant, K, was calculated to be 0.61 M^{-1} from the values of the intercept and the slope of the straight line. The value of ε_2 at any wavelength can be determined by using the values of ε_1 and

K. The absorption spectrum estimated in this way for $Cr(OAc)edta^{2-}$ is shown in Fig. 3, in which that of $Credta(H_2O)^-$ is also given for comparison.

Determination of the rate constants for Reaction (1) The acetate anation reaction was followed at 510 nm by the stopped-flow method. Under a pseudo-first order condition that the concentration of acetate was in a large excess over that of $Credta(H_2O)^-$, the conventional plot of $\log(D_t - D_e)$ vs. time gave a straight line, where D_t and D_e denote the absorbances at time t and infinite, respectively. The rate constants were calculated from the slope of the straight line and the value of K. The values obtained were 8.7 M^{-1} s^{-1} for k_f and 14 s^{-1} for k_b.

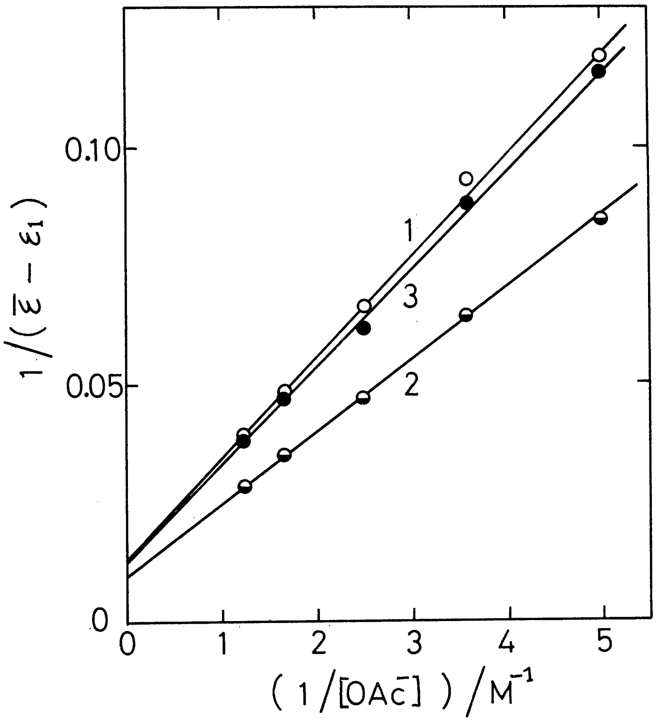

Fig. 2 The values of the left hand side of Eq. (3) as a function of the reciprocal acetate ion concentrations. The measurements were made at 490 (1), 510 (2) and 545 nm (3)

Chromium(III) complexes are known to be typically substitution-inert. However, both rate constants, k_f and k_b, obtained for chromium(III)-EDTA are remarkably large. It is known that the rate of exchange reaction between water molecule coordinated to metal ion and solvent water molecule increases by coordination of negative and/or dipolar ligands to the first coordination sphere$^{3)}$. It is also reported that the rate constant of water exchange in $Cr(H_2O)(NH_3)_5^{3+}$ is about 10^3 times larger than that of $Cr(H_2O)_6^{3+}$$^{4)}$. This is considered to be attributable to that metal-OH_2 bonding is weakened owing to the electron donation from the ligands to metal ion. In the case of $Credta(H_2O)^-$, the coordination of carboxyl groups and two nitrogen atoms brings about the concentration of negative charges and negative dipoles to the central chromium(III) ion. As the result, Cr-OH_2 bonding in $Credta(H_2O)^-$ will be loosened and the water molecule will be labilized. This effect may be, at least, one reason why the rate constants obtained in this work are so large.

The rapid formation of mixed ligand complexes $Cr(N_3)edta^{2-}$, and $Cr(OAc)hedta^-$, was also observed in this work, where hedta denotes N-hydroxyethylethylenediaminetriacetate. The details will be published elsewhere.

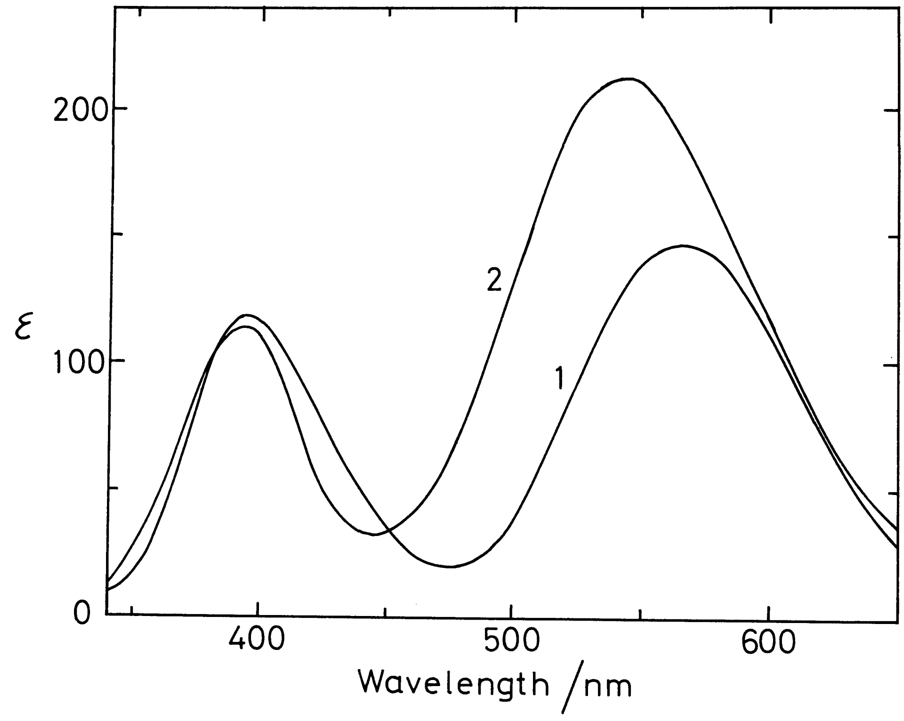

Fig. 3 Absorption spectra of $Cr(OAc)edta^{2-}$ (curve 1) and $Credta(H_2O)^-$ (curve 2)

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