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# Activation Parameters of the Electrode Reaction of *trans*-1,2-Cyclohexanediaminetetraacetatochromate(III) Complex

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In previous paper,[1] it was reported that in a solution of pH 4.6 the electrode reaction of *trans*-1,2-cyclohexanediaminetetraacetatochromate(II, III) complexes (Cr(II, III)-CyDTA) proceeds as

$$[\mathrm{Cr(III)\text{-}CyDTA}]^- + e \rightleftarrows [\mathrm{Cr(II)\text{-}CyDTA}]^{2-} \quad (1)$$

A mainly theoretical comparison between the kinetic parameters of the electrode reaction and those of the corresponding homogeneous reaction has been made by Marcus.[2] Although the value of the heat of activation of the electrode reaction is apparent and not absolute, as discussed by Vlček[3] and Tamamushi,[4] the activation parameters corrected for the electrical double layer seem to be useful for a comparison of the electron-transfer reaction at the electrode with those in the solution. The present communication presents the activation parameters of the reaction given by Eq. (1) which were obtained from potentiostatic measurements at various temperatures.

## Experimental

Sample solutions of Cr(III)-CyDTA with the supporting electrolyte containing 0.4M sodium chloride, 0.1M sodium acetate buffer and $2\times10^{-6}$M polyoxyethylene lauryl ether (LEO) were prepared in the same way as previously reported.[1]

For the measurements at 0°C, the temperature was kept constant with an ice-bath, and at 10, 15, 25, and 35°C, controlled by a thermostat. Other apparatus for the measurement were those described previously.[1]

## Results and Discussion

The polarograms of Cr(III)-CyDTA complex were measured at several temperatures and the results are given in Table 1. The slopes of log-plots of these polarograms showed that the electrode reaction of the Cr(II, III)-CyDTA system is diffusion-controlled at every temperature. A slope obtained from the Arrhenius plot of diffusion coefficients gave a reasonable value of the activation energy for diffusion. The kinetic parameters determined at various temperatures are given in Table 2.

TABLE 1. CHARACTERISTICS OF POLAROGRAPHIC REDUCTION OF 1mM Cr(III)-CyDTA AT VARIOUS TEMPERATURES, MEASURED IN THE SUPPORTING ELECTROLYTE SOLUTIONS OF pH 4.6 CONTAINING 0.4M NaCl, 0.1M ACETATE BUFFER AND $2\times10^{-6}$M LEO

| Temp. °C | $\bar{i}_d$ $\mu$A | $E_{1/2}$ V *vs.* SCE | Slope of log-plot mV | $D_0\times10^6$ $\mathrm{cm^2\cdot sec^{-1}}$ |
|---|---|---|---|---|
| 10 | −2.42 | −1.190 | 55 | 3.4 |
| 15 | −2.60 | −1.192 | 58 | 4.2 |
| 25 | −3.00 | −1.200 | 62 | 5.5 |
| 35 | −3.47 | −1.204 | 62 | 7.4 |

TABLE 2. MEASURED KINETIC PARAMETERS OF Cr(III)-CyDTA AT VARIOUS TEMPERATURES, OBTAINED IN THE SUPPORTING ELECTROLYTE SOLUTIONS OF pH 4.6 CONTAINING 0.4M NaCl, 0.1M ACETATE BUFFER AND $2\times10^{-6}$M LEO

| Temp. °C | $(E_0)_{ms}$ V *vs.* SCE | $(k_s)_{ms}$ $\mathrm{cm\cdot sec^{-1}}$ | $(\alpha_c)_{ms}$ | $(\alpha_a)_{ms}$ |
|---|---|---|---|---|
| 0 | −1.187 | 0.0045 | 0.36 | 0.78 |
| 10 | −1.195 | 0.0011 | 0.38 | 0.60 |
| 15 | −1.189 | 0.0093 | 0.39 | 0.57 |
| 20 | −1.194 | 0.018 | 0.36 | 0.61 |
| 25 | −1.198 | 0.029 | 0.33 | 0.67 |
| 35 | −1.204 | 0.051 | 0.33 | 0.68 |

The logarithmic values of the standard rate constant, $\log(k_s)_{ms}$, were plotted against $1/T$ in Fig. 1. The measured heat of activation, $(\Delta H_s^{\ast})_{ms}$, and the measured pre-exponential factor, $A_{ms}$, were obtained from the plot.

In Fig. 2, $\phi_2$ potentials, *i.e.*, potentials at the outer Helmholtz plane (OHP), are plotted against the electrode potential $E$ at 15, 25, and 35°C. At more negative potentials than *ca.* −1.18 V *vs.* SCE, $\phi_2$ potentials at those temperatures virtually coincide with each other.

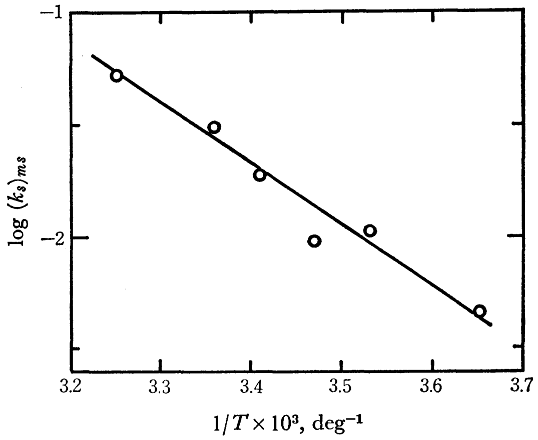

Fig. 1. The Arrhenius plot of $(k_s)_{ms}$ of Cr(III)-CyDTA obtained in the supporing electrolyte solutions of pH 4.6 containing 0.4 M NaCl, 0.1 M acetate buffer and $2\times10^{-6}$ M LEO. The values obtained are: $(\Delta H_s^{\ast})_{ms}=12$ kcal mole$^{-1}$ and $A_{ms}=10^{7.3}$ cm sec$^{-1}$.

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[1] N. Tanaka, T. Tomita, and A. Yamada, This Bulletin, **43**, 2042 (1970).

[2] R. A. Marcus, *Ann. Rev. Phys. Chem.*, **15**, 155 (1964).

[3] A. A. Vlček, *Collect. Czech. Chem. Commun.*, **24**, 3538 (1959).

[4] R. Tamamushi, *Rev. Polarog. (Kyoto)*, **10**, 1 (1962).

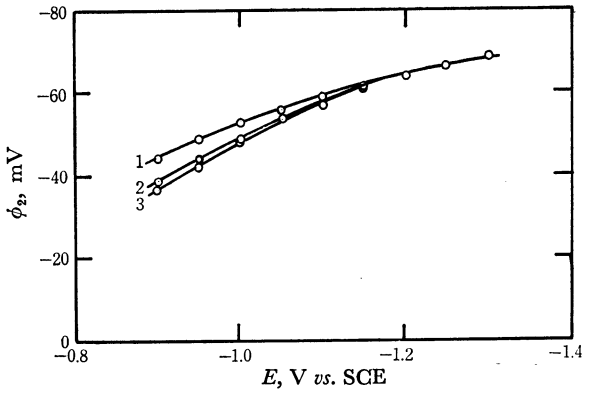

Fig. 2. $\phi_2$ potential as a function of the electrode potential $E$ at (1) 15°C, (2) 25°C, and (3) 35°C in a solution of pH 4.6 containing 0.4 M NaCl, 0.1 M acetate buffer and $2\times10^{-6}$ M LEO. $\phi_2$ values were estimated from the Gouy-Chapman theory.

Table 3. Corrected kinetic parameters of Cr(III)-CyDTA at various temperatures, obtained in the supporting electrolyte solutions of pH 4.6 containing 0.4M NaCl, 0.1M acetate buffer and $2\times10^{-6}$M LEO

| Temp. °C | $(E_0)_{corr}$ V vs. SCE | $(k_s)_{corr}$ cm·sec$^{-1}$ | $(\alpha_c)_{corr}$ | $(\alpha_a)_{corr}$ |
|---|---|---|---|---|
| 0 | −1.186 | 0.17 | 0.42 | 0.72 |
| 10 | −1.194 | 0.46 | 0.49 | 0.54 |
| 15 | −1.191 | 0.37 | 0.46 | 0.53 |
| 20 | −1.195 | 0.65 | 0.44 | 0.55 |
| 25 | −1.198 | 0.93 | 0.40 | 0.57 |
| 35 | −1.204 | 1.5 | 0.39 | 0.59 |

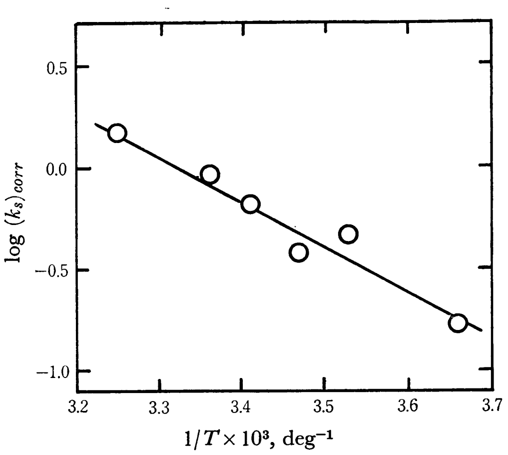

Fig. 3. The Arrhenius plot of $(k_s)_{corr}$ of Cr(III)-CyDTA obtained in the supporting electrolyte solutions of pH 4.6 containing 0.4 M NaCl, 0.1 M acetate buffer and $2\times10^{-6}$ M LEO. The values obtained are: $(\Delta H_s^{\ast})_{corr}=10$ kcal mole$^{-1}$ and $A_{corr}=10^{7.5}$ cm sec$^{-1}$.

The Frumkin correction can then be applied to the kinetic parameters using these $\phi_2$ potentials, assuming that the electron-transfer reaction plane (ERP) is the same as the closest approach of supporting electrolyte (OHP), and none of the chemical species present in the solution is adsorbed on the electrode. The parameters corrected in this way are given in Table 3. The corrected activation parameters are: $(\Delta H_s^{\ast})_{corr}=$ 10 kcal mol$^{-1}$ and $A_{corr}=10^{7.5}$ cm sec$^{-1}$ (Fig.3). There is a great difference between $(k_s)_{ms}$ and $(k_s)_{corr}$, as was reported previously.[1] On the other hand, $(\Delta H_s^{\ast})_{ms}$ is not so much influenced by the correction for the effect of double layer, which was already expected by Joshi *et al.*,[5] when $\phi_2$ potential is only slightly dependent on the temperature.

In conclusion, the contribution of the double layer effect to the heat of activation for Cr(II, III)-CyDTA system is relatively small although it can not be neglected.

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5) K. M. Joshi, W. Mehl, and R. Parsons, Trans. Symp. Electrode Prosesses, ed. by E. Yeager, (1961), p. 249.