The Oxidation-Reduction Potential of the System of Mn(II)EDTA-Mn(III)EDTA Complexes and the Stability Constant of Mn(III)EDTA Complex

By Nobuyuki TANAKA, Takashi SHIRAKASHI and Hiroshi OGINO

(Received January 26, 1965)

Recently Yoshino and his co-workers[1] have succeeded in preparation of a manganese(III) complex with ethylenediaminetetraacetate (EDTA), and its decomposition has been studied by several authors.[1-3] The thermodynamic properties of this complex, however, have not been reported yet. Meanwhile, the stability constant of the corresponding chromium(III) complex has been determined by Pecsok et al.[4] This urged us to undertake the determination of the stability constant of the manganese(III)-EDTA complex.

A preliminary investigation of the complex revealed that the change with time in the concentration of the Mn(III)EDTA complex can be followed by measuring the limiting current at the dropping mercury electrode, and the change with time in the equilibrium potential of the Mn(III)EDTA-Mn(II)EDTA system can be followed by measuring the zero-current potential at the rotated platinum electrode. In this paper, the standard oxidation-reduction potential of the Mn(III)EDTA-Mn(II)EDTA system and the stability constant of Mn(III)EDTA complex are presented.

Theoretical

The following reactions are considered:

$$\mathrm{Mn^{3+} + e \rightleftharpoons Mn^{2+}}, \qquad E^\circ_{\mathrm{Mn}} \tag{1}$$

$$\mathrm{MnY^{-} + e \rightleftharpoons MnY^{2-}}, \qquad E^\circ_{\mathrm{MnY}} \tag{2}$$

$$\mathrm{Mn^{2+} + Y^{4-} \rightleftharpoons MnY^{2-}}, \quad K_{\mathrm{Mn(II)Y}} \tag{3}$$

$$\mathrm{Mn^{3+} + Y^{4-} \rightleftharpoons MnY^{-}}, \quad K_{\mathrm{Mn(III)Y}} \tag{4}$$

where Y^{4-} is a quadrivalent anion of EDTA, E°_{Mn} and E°_{MnY} are the standard oxidation-reduction potentials for Eqs. 1 and 2 and $K_{\mathrm{Mn(II)Y}}$ and $K_{\mathrm{Mn(III)Y}}$ are the stability constants of MnY^{2-} and MnY^{-}, respectively.

From Eqs. 1 and 2, one obtains,

$$\mathrm{Mn^{3+} + MnY^{2-} \rightleftharpoons Mn^{2+} + MnY^{-}} \tag{5}$$

and

$$E^\circ_{\mathrm{Mn}} - E^\circ_{\mathrm{MnY}} = 0.0591 \log K^{\mathrm{Mn(III)}}_{\mathrm{Mn(II)}}, \text{ at } 25^\circ\mathrm{C} \tag{6}$$

where $K^{\mathrm{Mn(III)}}_{\mathrm{Mn(II)}}$ is the equilibrium constant of Eq. 5 given as,

$$K^{\mathrm{Mn(III)}}_{\mathrm{Mn(II)}} = \frac{[\mathrm{Mn^{2+}}][\mathrm{MnY^{-}}]}{[\mathrm{Mn^{3+}}][\mathrm{MnY^{2-}}]} = \frac{K_{\mathrm{Mn(III)Y}}}{K_{\mathrm{Mn(II)Y}}} \tag{7}$$

All the activity coefficients are assumed to be unity.

From Eqs. 6 and 7,

$$\log K_{\mathrm{Mn(III)Y}} = \frac{E^\circ_{\mathrm{Mn}} - E^\circ_{\mathrm{MnY}}}{0.0591} + \log K_{\mathrm{Mn(II)Y}}, \quad \text{at } 25^\circ\mathrm{C} \tag{8}$$

is obtained. In Eq. 8, the values of E°_{Mn} and $\log K_{\mathrm{Mn(II)Y}}$ are referred from the literature. The value of E°_{MnY} is obtained in the present experiment.

The equilibrium potential $E_{t=0}$ is expressed as,

---

1) Y. Yoshino, A. Ouchi, Y. Tsunoda and M. Kojima, *Can. J. Chem.*, **40**, 775 (1962).

2) Y. Yoshino, A. Ouchi and Y. Tsunoda, *Sci. Papers. Coll. Gen. Educ. Univ. Tokyo*, **13**, 27 (1963).

3) K. A. Schroeder and R. E. Hamm. *Inorg. Chem.*, **3**, 391 (1964).

4) R. L. Pecsok, L. D. Shields and W. P. Schaefer, ibid., **3**, 114 (1964).

$$E_{t=0}=E^{\circ}_{\mathrm{MnY}}-0.0591\log\frac{[\mathrm{Mn(II)Y}]_0}{[\mathrm{Mn(III)Y}]_0},\quad \text{at } 25^{\circ}\mathrm{C} \tag{9}$$

where t means the time after the dissolution of the Mn(III)EDTA complex, and the subscript 0 represents $t=0$. The value of E°_{MnY} in Eq. 9 can be determined from the plot of $E_{t=0}$ vs. $\log([\mathrm{Mn(II)Y}]_0/[\mathrm{Mn(III)Y}]_0)$.

Experimental

Mn(III)EDTA complex, $\mathrm{KMn(C_{10}H_{12}O_8N_2)2\cdot 5H_2O}$, was prepared according to the method of Yoshino.[1] In an aqueous solution, it decreases in concentration gradually due to the thermal decomposition. Therefore, it was weighed at each measurement and dissolved into the solution. The time when the complex was dissolved was considered to be the initial time of decomposition; the dissolution was readily completed by bubbling nitrogen gas through the solution. To avoid the effect of light, the measurements were made with a brown-colored cell under the safety lamp in a dark room. A DME and a rotated platinum electrode were inserted into an electrolysis cell; the former was connected to a Yanagimoto Galvarecorder Model GR-103 and the latter to a potentiometer to follow the change in the limiting current and the equilibrium potential as a function of time, respectively. The limiting current was measured at −0.5 V. vs. SCE. The pH of the solution was adjusted to be 4.63±0.03 with sodium acetate-acetic acid buffer and the ionic strength, to be 0.2 with potassium chloride.

Results and Discussion

The measurements were made with the solutions given in Table I at 25.0±0.1°C. In Fig. 1, the equilibrium potentials at time t, $E_{t=t}$, measured with the rotated platinum electrode were plotted against time t. Since the equilibrium potentials at $t=0$, $E_{t=0}$, are not accurately determined from Fig. 1, they were obtained by the following procedure.

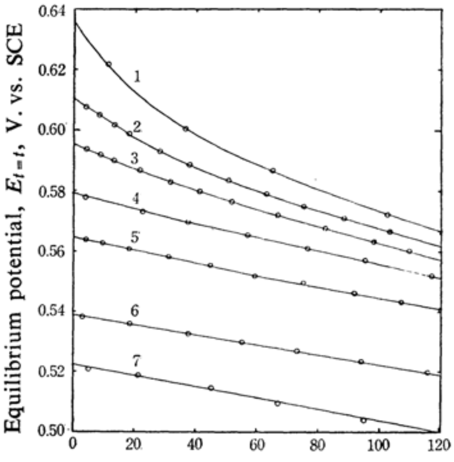

Fig. 1. $E_{t=t}$ as a function of time. Figures on the curves indicate experimental numbers given in Table I.

TABLE I. CONCENTRATIONS OF Mn(II)EDTA AND Mn(III)EDTA COMPLEXES IN THE SOLUTIONS*

Expt. No.	Concn. of Mn(II)Y mM	Concn. of Mn(III)Y** mM	pH
1	0.101_0	1.02_8	4.6_4
2	0.252_5	1.00_2	4.6_3
3	0.505_0	1.00_6	4.6_5
4	1.01_0	1.00_3	4.6_1
5	1.76_8	0.992_5	4.6_6
6	5.05_0	0.988_8	4.6_0
7	10.1_0	0.984_1	4.6_0

* Containing 0.05 M sodium acetate-acetic acid buffer and about 1 mM uncomplexed ethylenediaminetetraacetate, $\mu=0.2$ (KCl).

** Approximately 21 mg. of the complex were dissolved in 50 ml. of solution.

It was assumed that the decomposition product would have the same oxidation potential as the Mn(II)EDTA complex, and consequently, Eq. 9′ was derived from Eq. 9.

$$E_{t=t}=E^{\circ}_{\mathrm{MnY}}-0.0591\times \log\frac{[\mathrm{Mn(II)Y}]_0+[\mathrm{Mn(III)Y}]_0-[\mathrm{Mn(III)Y}]_t}{[\mathrm{Mn(III)Y}]_t} \tag{9'}$$

where the subscript t means $t=t$. In Eq. 9′ the value of $[\mathrm{Mn(III)Y}]_t$ was determined from the limiting current obtained with the DME at −0.5 V. vs. SCE; the limiting current of the Mn(III)EDTA complex was proved to be diffusion-controlled.* The values of $E_{t=t}$ were plotted against $\log\{([\mathrm{Mn(II)Y}]_0+[\mathrm{Mn(III)Y}]_0-[\mathrm{Mn(III)Y}]_t)/[\mathrm{Mn(III)Y}]_t\}$. Linear plots were obtained, and the more accurate values were determined for the equilibrium potential $E_{t=0}$ by the extrapolation of those plots to the points where the logarithmic terms equal to the values of $\log([\mathrm{Mn(II)Y}]_0/[\mathrm{Mn(III)Y}]_0)$.

According to Eq. 9, the values of $E_{t=0}$ determined by the above procedure were plotted against $\log([\mathrm{Mn(II)Y}]_0/[\mathrm{Mn(III)Y}]_0)$ which was calculated from Table I. Since this plot was very linear and its slope was found to be 57.2 mV., which was close to 59 mV. of the theoretical value, the above assumption and the determination of $E_{t=0}$ by the above procedure were considered to be valid and correct. From Fig. 2, the value of E°_{MnY} was determined to be 0.57_9 V. vs. SCE at the point of

---

* The datails will be published elsewhere.

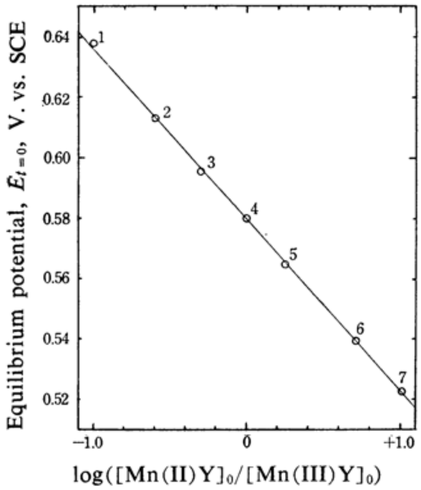

Fig. 2. Relation between equilibrium potential $E_{t=0}$ and $\log([Mn(II)Y]_0/[Mn(III)Y]_0)$ in Eq. 9. Figures on the plot indicate experimental numbers given in Table I.

$\log([Mn(II)Y]_0/[Mn(III)Y]_0)=0$. Introducing into Eq. 8 the values of $E^\circ_{Mn}=1.49$ V. vs. NHE,⁵⁾ $\log K_{Mn(II)Y}=13.64$⁶⁾ and $E^\circ_{MnY}=0.57_9$ V. vs. SCE (i. e. 0.82_3 V. vs. NHE), the value of $\log K_{Mn(III)Y}$ was calculated to be 24.9. As E°_{Mn} and E°_{MnY} are not determined under the identical condition, however, the value of the $\log K_{Mn(III)Y}$ may involve a somewhat minor error. The logarithmic stability constants of EDTA complexes of some transition metals are given in Table II. The value of $\log K_{Mn(III)Y}$ seems to be appropriate in comparison with those of other metals.

TABLE II. LOGARITHMIC STABILITY CONSTANTS OF EDTA COMPLEXES OF SOME TRANSITION METALS

Metal	Cr	Mn	Fe	Co
$\log K_{M(II)Y}$	13.6⁴⁾	13.64⁶⁾	14.33⁷⁾	15.71⁶⁾
$\log K_{M(III)Y}$	23.40⁴⁾	24.9	25.1⁷⁾	40.6⁸⁾

Summary

The standard oxidation-reduction potential of the system of Mn(II)EDTA-Mn(III)EDTA complexes has been determined to be $E^\circ_{MnY}=0.57_9$ V. vs. SCE from the potentiometric measurement with the rotated platinum electrode. From this value the logarithmic stability constant of the Mn(III)EDTA complex ($\log K_{Mn(III)Y}$) has been calculated to be 24.9 at 25.0°C and $\mu=0.2$.

The authors wish to thank the Ministry of Education for the financial support granted for this research.

Department of Chemistry
Faculty of Science
Tohoku University
Katahira-cho, Sendai

---

5) K. J. Vetter and G. Manecke, *Z. phys. Chem.*, **195**, 270 (1950).

6) H. Ogino, This Bulletin, **38**, 771 (1965).

7) G. Schwarzenbach and J. Heller, *Helv. Chim. Acta*, **34**, 576 (1951).

8) N. Tanaka and H. Ogino, This Bulletin, **38**, 1054 (1965).