BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 1563—1568 (1968)

An Experimental Study on the Faradaic Impedance of an Electrode Process with a Preceding Chemical Reaction

Kiyoshi MATSUDA and Reita TAMAMUSHI

The Institute of Physical and Chemical Research, Yamato-machi, Kita-adachi-gun, Saitama

(Received January 22, 1968)

The frequency dependence of the faradaic impedance and its phase angle of an electrode process with a preceding chemical reaction was studied with the Cd(II)-EDTA system. The experimental results were analyzed by means of Smith's equation, and the rate constant of the reaction, $Cd^{2+}+HY^{3-}\rightarrow CdY^{2-}+H^{+}$, was estimated to be equal to $2._{3}\times 10^{9}\ l\ mol^{-1}\ sec^{-1}$ at the ionic strength of 0.5 and at 25°C. In connection with this study, the faradaic impedance behavior of simple electrode processes was re-examined with the Cd(II)-, Pb(II)-, and Zn(II)-KCl systems.

The measurement of the faradaic impedance provides a useful method of analyzing the mechanism of electrode reactions. The frequency dependence of the faradaic impedance at reversible electrode potentials was applied by Randles and Somerton[1] and by Gerischer[2] to the determination of exchange currents of relatively simple electrode reactions. Sluyters *et al.* examined the frequency dependence of the faradaic impedance by using the complex impedance plane.[3] The relation between the peak currents on alternating current (a.c.) polarograms and the frequency of the superimposed alternating voltage was studied first

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[1] J. E. B. Randles, *Discussions Faraday Soc.*, **1**, 11 (1947); J. E. B. Randles and K. W. Somerton, *Trans. Faraday Soc.*, **48**, 937 (1952).

[2] H. Gerischer, *Z. physik. Chem.*, **202**, 302 (1953).

[3] M. Sluyters-Rehbach, D. J. Kooijman and J. H. Sluyters, "Polarography 1964," (Graham J. Hills, ed.), Vol. I, MacMillan, London (1966), p. 135.

by Breyer, Bauer and Hacobian⁴⁾ and later by Bauer and Elving.⁵⁾ The faradaic impedance of the polarographic reduction processes of cadmium, zinc, and thallium ions was investigated by Tamamushi and Tanaka as a function of the electrode potential;⁶⁾ they also reported that, in the case of cadmium ions, the faradaic impedances measured at 500, 1000, and 2000 cps were inversely proportional to the square root of the frequency.

The effect of preceding chemical reactions to the faradaic impedance was studied first by Gerischer in the absence of a direct current (d. c.) polarization.⁷⁾ Recently, theoretical equations were proposed by Smith describing the a. c. polarographic phase angle behavior for electrode processes with coupled chemical reactions,⁸⁾ and the equation was applied to the catalytic reduction of titanium-(IV) ions in the presence of chlorate ions.⁹⁾ The behavior of a. c. polarographic peak currents was applied by Aylward and Hayes to the determination of the rate constant of a coupled following reaction.¹⁰⁾ To authors' knowledge, however, experimental studies on the phase angle-frequency behavior of polarographic electrode processes with preceding reactions have not been reported previously.

This paper presents some experimental results on the faradaic impedance behavior of the polarographic reduction process of cadmium ions in acetate buffer solutions containing ethylenediaminetetraacetate (EDTA) and an excess of calcium chloride; the results are discussed in terms of Smith's equations.⁸⁾ In connection with this study, the faradaic impedance-frequency relationship of some simple electrode processes was re-examined in a wider frequency range.

Experimental

The electrolytic cell subjected to the impedance measurement is represented by the scheme,

DME	solution	MPE

where DME means a dropping mercury electrode and MPE a mercury pool electrode of a large surface area.

In the frequency range of 200—4000 cps, the resistance and capacitance components of the equivalent impedance of the cell were measured by an a. c. bridge similar to that described in a previous paper.¹¹⁾ At lower frequencies (30—200 cps), however, the cell admittance and its phase angle were measured by a potentiostatic a. c. polarograph.¹²⁾ The DME was negatively polarized by a d. c. potentiometer against the MPE in the solution. The amplitude of the superimposed alternating voltage was less than 5 mV in the bridge measurement and about 10 mV in the a. c. polarographic measurement, respectively. The faradaic impedance and phase angle reported in this paper are the values for the given constant surface area (0.035 cm²) of the DME at the end of the life of a mercury drop (drop time, 9 sec).

Vacuum-distilled mercury was used for the DME and the MPE. All solutions were prepared from analytical reagent grade chemicals and redistilled water. In each system except the Cd-EDTA a small amount of polyoxyethylene lauryl ether (LEO) was used as a maximum suppressor. The dissolved oxygen was expelled from the solution by bubbling nitrogen through the solution. All measurements were carried out in a water-thermostat of 25.0±0.1°C.

Results

Cd(II)-, Pb(II)-, and Zn(II)-KCl Systems. In the polarographic reduction of cadmium, lead, and zinc ions in 1 M potassium chloride solutions, both the resistance and the capacitance readings, R_m and C_m, of the bridge gave a peak at the summit potential, E_s, characteristic to the given electrode reaction. The series resistance, R_F, and the series capacitance, C_F, of the faradaic impedance, Z_F, were determined by the vector calculation from the R_m- and C_m-values under the assumption that the R_m- and C_m-values of the supporting electrolyte solution are equal to the resistance of the solution and the double layer capacity, respectively. The frequency dependence of Z_F, R_F, $1/(\omega C_F)$, and $\cot\phi(=\omega C_F R_F)$ of the Cd(II)-, Pb(II)-, and Zn-(II)-KCl systems is shown in Fig. 1, where these quantities are plotted as a function of $1/\sqrt{\omega}$ (ω, the angular frequency).

Cd(II)-EDTA System. The polarographic reduction of a cadmium ion (8 mM $Cd(NO_3)_2$) in an acetate buffer solution (pH=3.7; ionic strength, μ, adjusted to be 0.5 by potassium nitrate) containing 1.119×10^{-2} M EDTA and 0.1 M calcium chloride gives a kinetic current due to the dissociation reaction,

$$CdY^{2-} + H^{+} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Cd^{2+} + HY^{3-} \qquad (1)$$

where Y^{-4} means that tetravalent anion of EDTA; the aquo-cadmium and chloro- and acetato-complexes of cadmium then contribute to the charge-transfer process.¹³,¹⁴⁾ This reduction process

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4) B. Breyer, H. H. Bauer and S. Hacobian, *Australian J. Chem.*, **8**, 322 (1955).

5) H. H. Bauer and P. J. Elving, *Anal. Chem.*, **30**, 334 (1958); H. H. Bauer, D. L. Smith and P. J. Elving, *J. Am. Chem. Soc.*, **82**, 2094 (1960).

6) R. Tamamushi and N. Tanaka, *Z. physik. Chem., Neue Folge*, **21**, 89 (1959); *ibid.*, **28**, 158 (1961).

7) H. Gerischer, *Z. Elektrochem.*, **55**, 98 (1951).

8) D. E. Smith, *Anal. Chem.*, **35**, 602 (1963).

9) D. E. Smith, *ibid.*, **35**, 610 (1963).

10) G. H. Aylward and J. W. Hayes, *ibid.*, **37**, 195 (1965).

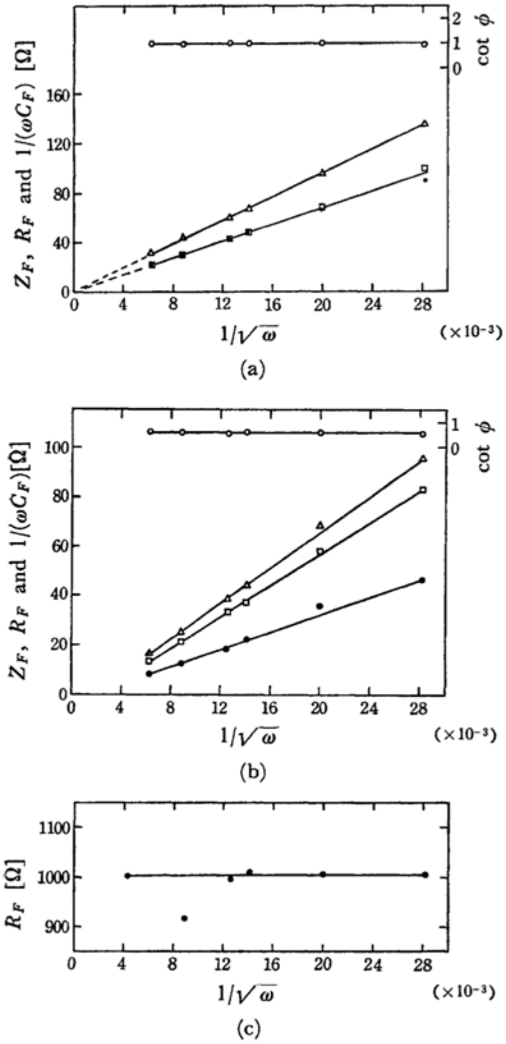
11) R. Tamamushi and K. Matsuda, *J. Electroanal. Chem.*, **12**, 436 (1966).

12) R. Tamamushi and K. Matsuda, This Bulletin, **41**, 1568 (1968).

13) N. Tanaka, R. Tamamushi and M. Kodama, *Z. physik. Chem., Neue Folge*, **14**, 141 (1958).

14) T. Fujisawa and N. Tanaka, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **87**, 965 (1966).

gave an a. c. polarogram and a phase angle change as shown in Fig. 2.



(a)

(b)

(c)

Fig. 1. Frequency dependence of Z_F (-△-), R_F (-●-), $1/(\omega C_F)$ (-□-) and cot ϕ(-○-) at the summit potential: (a), DME/0.5mM $CdSO_4$, 1M KCl, 2×10^{-6}M LEO/MPE; (b), DME/0.5 mM $Pb(NO_3)_2$, 1M KCl, 0.01N HCl, 5×10^{-6}M LEO/MPE; (c), DME/1 mM $Zn(NO_3)_2$, 1M KCl, 2×10^{-6} M LEO/MPE.

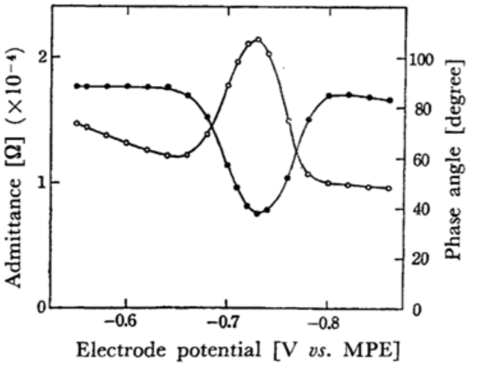


Fig. 2. A. c. polarogram (-○-) and phase angle change (-●-) at 30 cps of 8 mM $Cd(NO_3)_2$ in an acetate buffer solution (pH=3.7, μ=0.5) containing 1.119×10^{-2} M EDTA and 0.1 M $CaCl_2$.

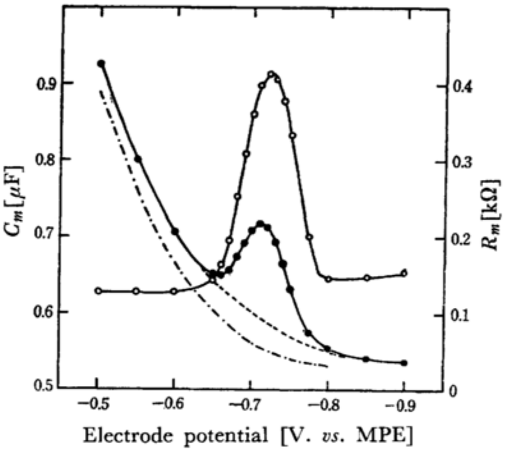


Fig. 3. Potential dependence of R_m(-○-) and C_m(-●-) of the DME/8 mM $Cd(NO_3)_2$, 1.119×10^{-2}M EDTA, 0.1 M $CaCl_2$, acetate buffer (pH=3.7, μ=0.5)/MPE system at 200 cps. (-·-: C_m-values of the supporting electrolyte solution (acetate buffer solution of pH=3.7 and μ=0.5 containing 1.119×10^{-2} M EDTA and 0.1 M $CaCl_2$)).

An example of the potential dependence of R_m and C_m at higher frequencies is reproduced in Fig. 3. The summit potential, being approximately independent of frequency, was −0.72—−0.73 V *vs.* MPE.

The C_m-values of the Cd(II)-EDTA system in the potential region outside the impedance peak did not coincide with the C_m-values of the supporting electrolyte solution (Fig. 3); this is probably due to the effect of the concentration of free EDTA anions on the double layer capacity. Therefore, the double layer capacity of the present system was estimated by the method of interpolation as shown by the dotted line in Fig. 3. In Fig. 4 the values of R_F, $1/(\omega C_F)$, and Z_F of the Cd(II)-EDTA system at the summit potential are plotted as a function of $1/\sqrt{\omega}$.

Discussion

The faradaic impedance of the electrode process is given by a series combination of the charge-transfer resistance which is independent of frequency, and the impedances due to the accompanying processes such as preceding and following chemical reactions, adsorption-desorption process, mass-transfer of reacting species, *etc.* According to the theory of a. c. polarization, these impedances have different

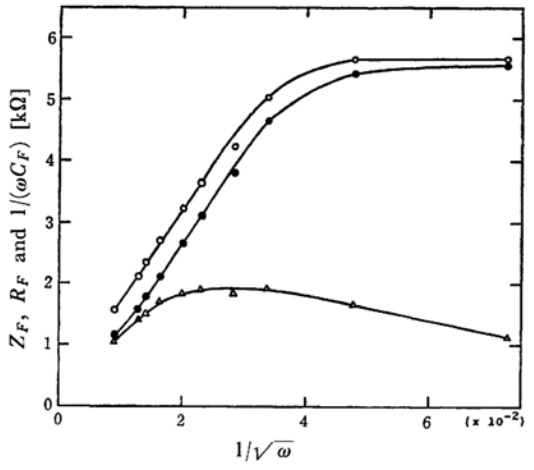


Fig. 4. Frequency dependence of Z_F (-○-), R_F (-●-) and $1/(\omega C_F)$ (-△-) at the summit potential of the DME/8 mM $Cd(NO_3)_2$, 1.119×10^{-2} M EDTA, 0.1 M $CaCl_2$, acetate buffer (pH=3.7, μ =0.5)/MPE system.

frequency dependence; for example, the Warburg impedance due to the diffusion process is expected to be proportional to $1/\sqrt{\omega}$, while the reaction impedance is a more complicated function of frequency.[15]

Cd(II)-, Pb(II)-, and Zn(II)-KCl Systems. The faradaic impedance of a simple electrode reaction mainly consists of the charge-transfer resistance, θ, and the Warburg impedance, Z_W; the faradaic impedance and its components are expected to be linear functions of $1/\sqrt{\omega}$.[15,16] This expectation is supported by the experimental results of Cd(II), Pb(II), and Zn(II) ions in 1 M potassium chloride solutions (Fig. 1).

The polarographic reduction of zinc ions in 1 M potassium chloride solutions is a well-known example of the quasi-reversible electrode reaction with the standard rate constant of the order of 10^{-3} cm/sec.[17] In such a quasi-reversible system, the charge-transfer resistance, θ, at the summit potential is expected to be much larger than the Warburg impedance, Z_W, even at low frequencies, and the resistance component, R_F, of the faradaic impedance at the summit potential will be approximately equal to θ and independent of frequency as shown in Fig. 1 (c).

The theory also suggests that the phase angle, ϕ, of a simple electrode process should be equal to $\pi/4$, being independent of frequency, for a totally reversible system, and it decreases with the decrease in the reversibility. The cot ϕ values of the reversible reduction of cadmium ions in potassium chloride solutions, as given in Fig. 1 (a), are in good agreement with the theory. In the Pb(II)-KCl system, however, the cotϕ value at each frequency studied was smaller than unity inspite of the high reversibility of the system (Fig. 1 (b)); this anomaly in the faradaic impedance may be attributed to the adsorption of the reacting species on the electrode surface.[18,19]

Cd(II)-EDTA System. In the polarographic reduction of the Cd(II)-EDTA system, the plots of Z_F, R_F, and $1/(\omega C_F)$ against $1/\sqrt{\omega}$ gave significant deviations from the linearity at lower frequencies (Fig. 4). These deviations can be explained in terms of the contribution of the reaction impedance due to the preceding chemical reaction (1).

According to Smith's treatment,[8] the cotϕ of the electrode reaction,

$$\mathrm{Y} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \mathrm{O} \tag{2}$$

$$\mathrm{O} + n\mathrm{e} \rightleftharpoons \mathrm{R} \tag{3}$$

is given by the equation,

$$\cot\phi = \frac{\dfrac{\sqrt{2\omega}}{\lambda} + \dfrac{1}{(1+\mathrm{e}^j)}\left\{\dfrac{1}{1+K}\left[\dfrac{(1+g^2)^{1/2}+g}{1+g^2}\right]^{1/2} + \dfrac{K}{1+K} + \mathrm{e}^j\right\}}{\dfrac{1}{(1+\mathrm{e}^j)}\left\{\dfrac{1}{1+K}\left[\dfrac{(1+g^2)^{1/2}-g}{1+g^2}\right]^{1/2} + \dfrac{K}{1+K} + \mathrm{e}^j\right\}} \tag{4}$$

where

$K = k_f/k_b, \quad g = l/\omega, \quad l = k_f + k_b,$

$\lambda = k_s f_O{}^{\alpha} f_R{}^{\beta} (D_O{}^{-\beta} D_R{}^{-\alpha})^{1/2} (\mathrm{e}^{-\alpha j} + \mathrm{e}^{+\beta j}),$

$\alpha + \beta = 1, \quad j = nF(E - E^r{}_{1/2})/(\boldsymbol{R}T)$

k_f, k_b: forward and backward rate constants, respectively, of reaction (2)

k_s: standard rate constant of reaction (3)

f_O, f_R: activity coefficients of O and R, respectively

D_O, D_R: diffusion coefficients of O and R, respectively

α, β: transfer coefficients

E: electrode potential

$E^r{}_{1/2}$: reversible half wave potential of reaction (3)

The impedance behavior of the Cd(II)-KCl

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15) P. Delahay, "Advances in Electrochemistry and Electrochemical Engineering," Vol. I, Chap. 5, Interscience Publishers, New York (1961); K. J. Vetter, "Elektrochemische Kinetik," Springer-Verlag, Berlin (1961).

16) H. Matsuda, *Z. Elektrochem.*, **62**, 977 (1958).

17) N. Tanaka and R. Tamamushi, *Electrochim. Acta*, **9**, 963 (1964).

18) M. Senda and P. Delahay, *J. Phys. Chem.*, **65**, 1580 (1961).

19) M. Sluyters-Rehbach, B. Timmer and J. H. Sluyters, *J. Electroanal. Chem.*, **15**, 151 (1967).

TABLE 1. RATE CONSTANTS OF THE FORMATION REACTION OF CADMIUM-EDTA, $Cd^{2+}+HY^{3-} \rightarrow CdY^{2-}+H^+$, IN ACETATE BUFFER SOLUTIONS AT 25°C

Ionic strength	Rate const. $l\ mol^{-1}\ sec^{-1}$	Method[b]	Reference
0.1	8.5×10^8	$E_{1/2}$	Koryta, Zábranský[20]
0.1	6.4×10^9	$E_{1/2}$	Aylward, Hayes[10]
0.5	4.0×10^9	$E_{1/2}$	Aylward, Hayes[10]
0.5[a]	5.3×10^8	$E_{1/2}$	Aylward, Hayes[10]
0.5[a]	6.1×10^8	f. a.	Aylward, Hayes[10]
0.5[a]	2.3×10^9	k. c.	Fujisawa, Tanaka[14]
0.5[a]	$2._3\times10^9$	ϕ	This study

a) Containing calcium ions.
b) $E_{1/2}$ refers to the analysis of the half wave potential, f. a., to the faradaic admittance measurement, k. c., to the kinetic current behavior, and ϕ, to the phase angle behavior, respectively.

system suggests that the value of $(\sqrt{2\omega}/\lambda)$ of the present system can safely be neglected against the following term in the numerator of Eq. (4); this is also supported by the behavior of R_F and $1/(\omega C_F)$ of the Cd(II)-EDTA system at higher frequencies as shown in Fig. 4. Therefore, the cot ϕ is represented by a simplified equation:

$$\cot\phi = \frac{\left[\dfrac{(1+g^2)^{1/2}+g}{1+g^2}\right]^{1/2} + K + (1+K)e^j}{\left[\dfrac{(1+g^2)^{1/2}-g}{1+g^2}\right]^{1/2} + K + (1+K)e^j} \tag{5}$$

Figure 5 presents the frequency dependence of cot ϕ at the summit potential ($E_s=-0.72$ V *vs.* MPE for 70—2000 cps, and $E_s=-0.73$ V *vs.* MPE for 30 cps), and the theoretical curves for $l=500$, 1000, and 2000 calculated by Eq. (5) with $K=[Cd]/[CdY^{2-}]=10^{-3.67}$ ([Cd], the total concentration of the electroactive cadmium species) and $E^r_{1/2}=-0.678$ V *vs.* MPE. The K-value was determined by using the equilibrium constants of EDTA, EDTA-complexes of cadmium and calcium ions, and chloro- and acetato-complexes of cadmium as given in the literature,[14] and $E^r_{1/2}$ was assumed to be equal to the half wave potential of Cd(II) in an acetate buffer solution (pH=3.7, $\mu=0.5$ adjusted by potassium nitrate) containing 0.1 M calcium chloride.

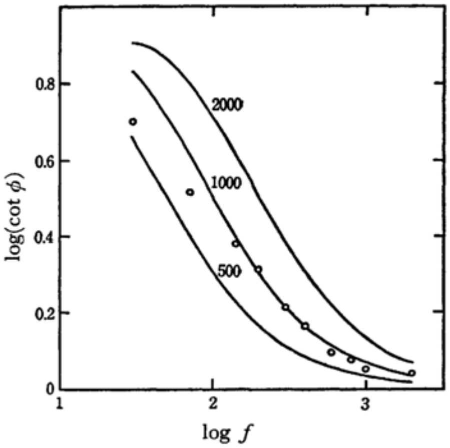

Fig. 5. Relation between log (cot ϕ) and log f (f, frequency) at the summit potential of the Cd-EDTA system; the circles represent the experimental values, and the solid lines correspond to the theoretical curves calculated by Eq. (5) with the l-values given on each curve.

This result shows that the best fit between the experimental and theoretical curves is obtained with $l=1000$. Because of the very small value of K of the present system, the l-value is practically equal to the pseudo first-order rate constant of the formation reaction of CdY^{2-} from the electroactive cadmium species and HY^{3-}, *i. e.*, $l=k'_2[HY^{3-}]=1000$, from which the value of k'_2 is estimated to be $2._4\times10^8\ l\ mol^{-1}\ sec^{-1}$. The rate constant, k'_2, thus determined should be regarded as the overall rate constant of the formation reaction related to the total concentration of the electroactive cadmium species (Cd^{2+}, $CdCl^+$, $CdCl_2$, and $CdOAc^+$). It is generally assumed, however, that only the aquo-cadmium ions react with HY^{3-} to form CdY^{2-}. If this simplified assumption is accepted, the k'_2-value must be multiplied by the factor of $(1+\beta_{CdCl}[Cl^-]+\beta_{CdCl_2}[Cl^-]^2+\beta_{CdOAc}[OAc^-])$, where β_i represents the overall formation constant of the i-species, in order to obtain the rate constant, k_2, corrected for chloro- and acetato-complexes of cadmium; the corrected k_2-value was thus determined to be $2._3\times10^9\ l\ mol^{-1}\ sec^{-1}$.

The rate constants for the formation of cadmium-EDTA have been reported by several authors; some examples of the k_2-values are listed in Table 1. Koryta and Zábranský determined the k_2-value by analyzing the d. c. polarograms of the anodic dissolution of cadmium amalgam in acetate buffer solutions containing EDTA.[20] The same

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[20] J. Koryta and Z. Zábranský, *Collection Czechoslov. Chem. Commun.*, **25**, 3153 (1960).

method of analysis was examined by Aylward and Hayes;[10] they also applied the faradaic admittance measurement of the anodic dissolution of cadmium amalgam followed by the formation reaction of cadmium-EDTA to the determination of the k_2-values. On the other hand, Tanaka *et al.* studied the kinetic current behavior of cadmium-EDTA at a DME in acetate buffer solutions containing calcium ions;[13,14] they determined the rate constant, k_1, of the dissociation reaction of CdY^{2-}, and then calculated the k_2-value by using the equilibrium constant of reaction (1). A survey of Table 1 shows that our figure is in good agreement with that of Fujisawa and Tanaka.[14]

Finally, the a. c. polarographic studies with the phase angle measurement is concluded to help in analyzing electrochemical mechanisms and in the determination of the rate constant of a coupled preceding reaction.

The authors wish to thank Professor N. Tanaka of Tohoku University and Dr. T. Fujisawa of Yamagata Technical College for valuable discussion.