PROGRESS IN POLAROGRAPHY

Edited by

P. ZUMAN and L. MEITES

I. M. KOLTHOFF

VOLUME III

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To J. Heyrovský, R. Brdička, and B. Breyer
in gratitude for their roles in developing electrochemistry
to its present state

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PREFACE

During the decade that has elapsed since the publication of the first two volumes of this series, polarography and the other electroanalytical techniques related to it have undergone expansion and development that have both deepened our theoretical knowledge and broadened the experimental basis for further advances. The progress in instrumentation that has been made in this decade led to the development of new, sophisticated, and often highly specialized techniques, which in some cases have provided more straightforward or accurate approaches to systems already well characterized by dc polarography, and in other cases have revealed phenomena difficult or even impossible to detect by classical techniques.

The present volume deals with a number of aspects of polarography that are of special interest in current research. Two contemporary electrochemical problems on which much attention is focused—the formation and reactions of radicals and radical ions, and the effects of the electrical double layer on electrode processes—are discussed by Doz. B. Kastening and Dr. S. G. Mairanovskii, respectively. In stripping techniques, which have assumed great importance in trace analysis, the compounds that deposited metals may form with each other and with the mercury into which they are deposited are of great importance, and these and the techniques by which they have been identified and studied are reviewed by Professor M. T. Kozlovsky and Mme. A. Zebreva. Interest in inorganic polarography has been divided between studies of labile and substitution-inert complexes; studies of the former group are surveyed by Professor R. Tamamushi and Dr. G. Satô. Finally, the question of how to interpret a given set of polarographic data, with special reference to the effects of varying the pH, is discussed by Professor P. Zuman.

This is by no means an exhaustive selection of topics of current interest. We believe it illustrates the breadth of modern polarography without unduly emphasizing any one narrow area, and we have chosen to restrict the number of fields included so that each could be discussed fully while keeping the size of the volume within reasonable bounds.

Since the first two volumes of this series were published, three of those who contributed to them have been lost to the polarographic family. The deaths of J. Heyrovský, R. Brdička, and B. Breyer have left us all poorer.

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CHAPTER I

APPLICATION OF POLAROGRAPHY AND RELATED ELECTROCHEMICAL METHODS TO THE STUDY OF LABILE COMPLEXES IN SOLUTION

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I. Introduction

Historically, the polarographic study of inorganic complexes goes back to the pioneering work of von Stackelberg and von Freyhold (81) and of Lingane (46). The classic method of analysis is thoroughly treated by Kolthoff and Lingane in their famous monograph on polarography. Since then, both theory and methodology of polarography and related electrochemical techniques have made remarkable progress, and now these techniques enjoy wide application to the study of complexes in solution. Some of the general developments are presented and discussed by Crow and Westwood (14, 15) and by Crow (13) in their recent publications. Excellent reviews have also been published by Vlček (117, 118) on the relationship between the electrochemical reactivity and the structure of inert complexes and by Koryta (39) on the electrochemical kinetics of metal complexes.

This chapter concerns a theoretical treatment of the electrode reaction of labile complexes and its application to the study of equilibria and kinetics of labile complexes in solution. In addition to conventional polarography, some of the related techniques, such as potentiostatic, galvanostatic, and impedance measurements, are included as well. This article is not intended to be a comprehensive review of the given subjects; topics are chosen and treated on the basis of the authors' personal interests.

II. Theoretical Treatment of the Electrode Reaction of Labile Complexes

A. *Electrode Reaction and Equilibrium Potentials of Labile Complexes*

Labile complex species $M^{m+}L_i$ ($i = 0, 1, 2, \ldots, p, \ldots, \mu$) are generally subjected to the following stepwise equilibria in solution:

$$M^{m+}L_i + L \rightleftharpoons M^{m+}L_{i+1} \; (i = 0, 1, 2, \ldots, p, \ldots, \mu - 1) \tag{1a}$$

where $i = 0$ refers to a simple metal ion M^{m+} and μ is the maximum number of ligands L coordinated with M^{m+}. In this article the charge of each complex species and that of L are omitted in order to avoid complications in representing chemical species.

Let us assume that the complex species $M^{m+}L_p$ is involved in the charge transfer process as given by Eq. 1b:

$$M^{m+}L_p + ze \rightleftharpoons M^{(m-z)+}L_q + (p - q)L \tag{1b}$$

If the reduced form of $M^{m+}L_p$ is also a labile complex species, another set of stepwise equilibria should be considered with respect to the reduced species:

$$M^{(m-z)+}L_j + L \rightleftharpoons M^{(m-z)+}L_{j+1} \; (j = 0, 1, 2, \ldots, q, \ldots, \nu - 1) \tag{1c}$$

ν being the maximum number of L coordinated with metal ion $M^{(m-z)+}$.

The overall electrode reaction of a labile complex species consists of these three processes (Eq. 1a–c), and it offers a typical example of the charge transfer process coupled with homogeneous chemical reactions. The contribution of heterogeneous coupled reactions is not discussed in this article.

The equilibrium potential E_e of the $M^{m+}L_i/M^{(m-z)+}L_j$ redox system is given by Eq. 2 after the Nernst equation:

$$E_e = E_p{}^{\ominus} + \frac{RT}{zF} \ln \frac{[M^{m+}L_p]}{[M^{(m-z)+}L_q][L]^{(p-q)}} \tag{2}$$

where $E_p{}^{\ominus}$ is the standard potential corresponding to the charge transfer process of Eq. 1b and [ ] represents the concentration of each species in the bulk of the solution. The effect of activity coefficients is neglected for the sake of simplicity.

Introducing the total concentration c_{ox} of the oxidized form and that of the reduced form c_{red},

$$\left.\begin{aligned} c_{\text{ox}} &= \sum_{i=0}^{\mu} [M^{m+}L_i] \\ c_{\text{red}} &= \sum_{j=0}^{\nu} [M^{(m-z)+}L_j] \end{aligned}\right\} \tag{3}$$

we obtain Eq. 4, representing the equilibrium potential in terms of c_{ox} and c_{red}:

$$E_e = (E^{\ominus})_B + \frac{RT}{zF} \ln \frac{c_{\text{ox}}}{c_{\text{red}}} + \frac{RT}{zF} \ln \frac{F_0^{\text{ox}}([L]=1)}{F_0^{\text{red}}([L]=1)} - \frac{RT}{zF} \ln \frac{F_0^{\text{ox}}([L])}{F_0^{\text{red}}([L])} \tag{4}$$

where $(E^{\ominus})_B$ is the standard potential corresponding to the standard state of the overall electrode reaction ($c_{\text{ox}} = c_{\text{red}} = [L] =$ unit concentration), and related to $E_p{}^{\ominus}$ by the relation

$$(E^{\ominus})_B = E_p{}^{\ominus} + \frac{RT}{zF} \left\{ \ln \frac{\beta_p^{\text{ox}}}{F_0^{\text{ox}}([L]=1)} - \ln \frac{\beta_q^{\text{red}}}{F_0^{\text{red}}([L]=1)} \right\} \tag{5}$$

The functions $F_0^{\text{ox}}([L])$ and $F_0^{\text{red}}([L])$ are represented by

$$F_0^{\text{ox}}([L]) \equiv 1 + \beta_1^{\text{ox}}[L] + \beta_2^{\text{ox}}[L]^2 + \cdots + \beta_\mu^{\text{ox}}[L]^\mu = \sum_{i=0}^{\mu} \beta_i^{\text{ox}}[L]^i \tag{6a}$$

$$F_0^{\text{red}}([L]) \equiv 1 + \beta_1^{\text{red}}[L] + \beta_2^{\text{red}}[L]^2 + \cdots + \beta_\nu^{\text{red}}[L]^\nu = \sum_{j=0}^{\nu} \beta_j^{\text{red}}[L]^j \tag{6b}$$

β_i^{ox} and β_j^{red} being the overall stability constants of $M^{m+}L_i$ and $M^{(m-z)+}L_j$, respectively, as defined by Eq. 7a and b:

$$\beta_0^{\text{ox}} = 1, \qquad \beta_i^{\text{ox}} = \frac{[M^{m+}L_i]}{[M^{m+}][L]^i} \; (i = 1, 2, \ldots, \mu) \tag{7a}$$

$$\beta_0^{\text{red}} = 1, \qquad \beta_j^{\text{red}} = \frac{[M^{(m-z)+}L_j]}{[M^{(m-z)+}][L]^j} \; (j = 1, 2, \ldots, \nu) \tag{7b}$$

The values of $F_0^{\mathrm{ox}}([\mathrm{L}] = 1)$ and $F_0^{\mathrm{red}}([\mathrm{L}] = 1)$ are numerically identical with

$$\sum_{i=0}^{\mu} \beta_i^{\mathrm{ox}} \quad \text{and} \quad \sum_{j=0}^{\nu} \beta_j^{\mathrm{red}}$$

respectively.

B. Faradaic Current

The faradaic current density I attributable to the charge transfer process of Eq. 1b is given by Eq. 8 when a positive sign is assigned to the cathodic current*:

$$\frac{I}{zF} = \bar{k}_p{}^c\,[\mathrm{M}^{m+}\mathrm{L}_p]_s - \bar{k}_p{}^a\,[\mathrm{M}^{(m-z)+}\mathrm{L}_q]_s\,[\mathrm{L}]_s^{(p-q)} \tag{8}$$

where $[\;]_s$ denotes the concentration at the electrode surface and $\bar{k}_p{}^c$ and $\bar{k}_p{}^a$ are the electrochemical rate constants of the cathodic and the anodic processes, respectively, of the charge transfer process of Eq. 1b. The electrochemical rate constant can be expressed by Eq. 9 as a function of the electrode potential E referred to a given reference electrode:

$$\left.\begin{aligned} \bar{k}_p{}^c &= k_p{}^c \exp\left\{-\frac{\alpha_p zF}{RT}E\right\} \\ \bar{k}_p{}^a &= k_p{}^a \exp\left\{\frac{(1-\alpha_p)zF}{RT}E\right\} \end{aligned}\right\} \tag{9}$$

where α_p is the cathodic transfer coefficient, $k_p{}^c$ and $k_p{}^a$ are the cathodic and anodic rate constants, respectively, at $E = 0$, and all the other symbols have their usual meanings. The double-layer effect on the electrode kinetics of metal complexes has been discussed by Koryta (39) and is ignored in this article.

At the dynamic equilibrium of the electrode reaction, which is defined as the state in which no net current is flowing, the electrode potential and the surface concentrations should be equal to E_e and the bulk concentrations, respectively, and the following relations must be satisfied:

$$k_p{}^c\,[\mathrm{M}^{m+}\mathrm{L}_p]\exp\left\{-\frac{\alpha_p zF}{RT}E_e\right\} = k_p{}^a\,[\mathrm{M}^{(m-z)+}\mathrm{L}_q][\mathrm{L}]^{(p-q)}\exp\left\{\frac{(1-\alpha_p)zF}{RT}E_e\right\} \tag{10}$$

or

$$k_p{}^c c_{\mathrm{ox}}[\mathrm{L}]^p \frac{\beta_p^{\mathrm{ox}}}{F_0^{\mathrm{ox}}([\mathrm{L}])}\exp\left\{-\frac{\alpha_p zF}{RT}E_e\right\} = k_p{}^a c_{\mathrm{red}}[\mathrm{L}]^p \frac{\beta_q^{\mathrm{red}}}{F_0^{\mathrm{red}}([\mathrm{L}])}\exp\left\{\frac{(1-\alpha_p)zF}{RT}E_e\right\} \tag{11}$$

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* We adopt this sign convention in this chapter in order to avoid confusion with the existing convention in polarography. Theoretically, however, the reverse convention may be preferable.