Electrochemical analysis of metal complexes

Promotor: dr. J. Lyklema, hoogleraar in de Fysische chemie,
met bijzondere aandacht voor de Grensvlak- en Kolloïdchemie
Co-promotor: dr. H.P. van Leeuwen, universitair hoofddocent

Hans G. de Jong

Electrochemical analysis of metal complexes

Proefschrift
ter verkrijging van de graad van
doctor in de landbouwwetenschappen,
op gezag van de rector magnificus,
dr. C.C. Oosterlee,
in het openbaar te verdedigen
op woensdag 9 december 1987
des namiddags te vier uur in de aula
van de Landbouwuniversiteit te Wageningen

CONTENTS

1. INTRODUCTION 1

2. VOLTAMMETRY OF METAL COMPLEX SYSTEMS WITH DIFFERENT DIFFUSION COEFFICIENTS OF THE SPECIES INVOLVED PART I. Analytical approaches to the limiting current for the general case including association/dissociation kinetics 11

3. VOLTAMMETRY OF METAL COMPLEX SYSTEMS WITH DIFFERENT DIFFUSION COEFFICIENTS OF THE SPECIES INVOLVED PART II. Behaviour of the limiting current and its dependence on association/dissociation kinetics and lability 27

4. VOLTAMMETRY OF METAL COMPLEX SYSTEMS WITH DIFFERENT DIFFUSION COEFFICIENTS OF THE SPECIES INVOLVED PART III. The current-potential relation for the general case including association/dissociation kinetics 40

5. PULSE POLAROGRAPHIC SPECIATION OF HEAVY METAL/POLYELECTROLYTE SYSTEMS 50

6. CONDUCTOMETRIC ANALYSIS OF THE COMPETITION BETWEEN MONOVALENT AND DIVALENT COUNTERIONS IN THEIR INTERACTION WITH POLYELECTROLYTES 59

SUMMARY 69

SAMENVATTING 72

CURRICULUM VITAE 75

DANKWOORD 76

STELLINGEN

1. Voor voltammetrische metaalspeciatie is de grootte van de diffusiecoëfficiënt van het ligand vrijwel altijd een noodzakelijk gegeven.

Dit proefschrift, hoofdstuk 2.

2. De door De Lurdes Simoes Gonçalves et al. gegeven interpretatie van voltammetrische experimenten aan metaal/kolloïd complexen is onzorgvuldig, omdat op onvoldoende gronden een eventuele bijdrage van gebonden metaal ionen aan de stroom is verwaarloosd.

M. de Lurdes Simoes Gonçalves, L. Sigg en W. Stumm, Environ. Sci. Technol., 19(1985)141.

Dit proefschrift, hoofdstuk 3.

3. In het conductometrisch deel van hun studie naar de interactie van zink ionen met polymethacrylaat ionen in kaliumnitraat, besteden Kolawole en Olayemi ten onrechte geen aandacht aan het vrijkomen van gebonden kalium ionen als gevolg van toevoeging van zink ionen.

E.G. Kolawole en J.Y. Olayemi, Macromolecules, 14(1981)1050.

Dit proefschrift, hoofdstuk 6.

. De door Britz voorgestelde verfijning van de berekening van gradiënten op basis van numerieke verdelingsfuncties, verkregen door gebruik van de Crank-Nicolson methode, is zinloos.

D.Britz, Anal. Chim. Acta, 193(1987)277.

. De veronderstelling van Wells et al. dat het contactoppervlak van N-alkyl-enzamiden op ODS kolommen niet alleen door de structuur van deze verbindingen epaald wordt, wekt twijfel omtrent de door hen opgestelde structuur-retentie elaties.

.J.M. Wells, C.R. Clark en R.M. Patterson, J. Chromatogr., 235(1982)61.

. Het is niet juist om a priori te beweren dat in geval van tensammetrische etectie in vloeistofstromen een grotere gevoeligheid ook een groter lineair ereik betekent, omdat het ruisniveau onafhankelijk is van de aard van de te etecteren verbinding.

. Lankelma en H. Poppe, J.Chromatogr. Sci., 14(1976)310.

7. De veronderstelling van Lovrić en Branica dat hun differentiële pulsvoltammetrisch signaal door een te grote integratietijd van het analoge geheugen in het meetinstrument is verstoord, is vrijwel zeker onjuist.

M. Lovrić en M. Branica, J. Electroanal. Chem., 183(1985)107.

8. Bij modelberekeningen aan fotochemische systemen voor waterstofproductie uit water verricht door Miller et.al., wordt de oxydatie van waterstof aan het katalysator oppervlak ten onrechte a priori verwaarloosd.

D.S. Miller, A.J. Bard, G. Mclendon
en J. Ferguson, J. Am. Chem. Soc. 103(1981)5336.

J.M. Kleijn, Proefschrift, Landbouwuniversiteit, Wageningen, 1987,
hoofdstuk 6.

9. Indien auteurs van studieboeken met vraagstukken geen antwoordenlijst menen te moeten opnemen en daar als belangrijkste reden voor aanvoeren dat de methode waarmee het antwoord verkregen wordt belangrijker is dan het antwoord zelf, is het consequenter om een "methodenlijst" op te nemen.

P.J. van Duin en A. Waasdorp, Analytische Chemie; vraagstukken, Agon Elsevier, Amsterdam, 1970.

10. De volstrekte openheid van parlementaire enquetes betreffende vermeend wanbeleid kan een ondermijnend effect op de publieke opinie hebben.

11. De term "permanent" waarmee kappers een bepaalde haarbehandeling aanduiden, heeft veeleer betrekking op de frequentie van het kapsalonbezoek dat uit die behandeling voortvloeit dan op de duurzaamheid van het resultaat.

Proefschrift Hans G. de Jong
Electrochemical Analysis of Metal Complexes
Wageningen, 9 december 1987

CHAPTER 1

INTRODUCTION

GENERAL

Nowadays, heavy metals are used in a wide variety of industrial products such as paints (Pb,Cd), gasoline (Pb) and batteries (Pb,Cd,Ni,Zn). As a consequence of the industrial applications, the level of a number of heavy metals in the environment increases. Since even at low concentrations, these metals are harmful to living organisms, their accumulation in certain parts of the environment has become a well-known and serious problem [1].

The bioaccumulation and toxicity of heavy metals are mainly governed by their and nature and chemical state. Heavy metals show a tendency to form complexes with organic and inorganic ligands. This tendency is the mechanism of their toxic action e.g. interaction of heavy metals and natural polyacids such as RNA and DNA probably may account for their mutagenic and carcinogenic effects. Another important aspect of the tendency to form complexes is that naturally occurring chelating agents such as fulvic and humic acids appear to render heavy metals to be less toxic [1].

The serious pollution hazard of heavy metals demands reliable analytical techniques, which allow the detection of the very low concentration levels usually encountered in natural samples. Besides, methodes are required which specify the different chemical complex forms of a particular metal ('speciation'). The most popular techniques in the analysis of heavy metals are Atomic Absorption Spectroscopy (AAS) and voltammetry [2].

The detection limit of both techniques is sufficiently low for most of the environmental samples, however only voltammetry allows direct speciation in the original sample.

In natural samples, a great number of ligands such as proteins, humics, and fulvics are much larger than the uncomplexed metal ion. For such systems, voltammetry is still in its infancy due to a complete lack of a rigorous theory. The present study is concerned with developing such a theory against the background of applying voltammetry as a tool for heavy metal speciation.

For the solution of a great deal of analytical problems the analytical chemist not only needs a thorough understanding of the method used, but also

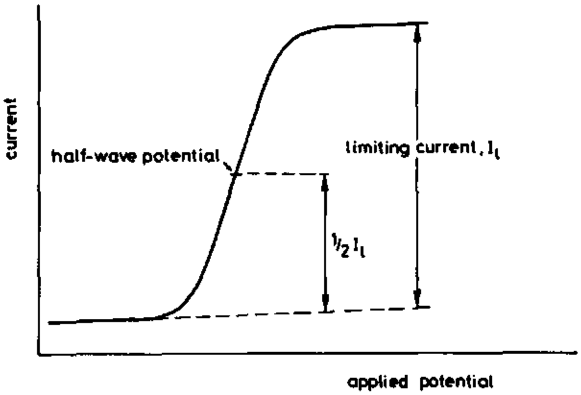

FIGURE 1 : A typical voltammogram recorded under polarographic or stationary state conditions.

of the physical chemistry of the system studied. This is particularly true for the analysis of heavy metals in natural samples. The natural complexing agents such as fulvic and humic acids are polyfunctional ligands and exhibit polyelectrolyte-like behaviour in their interaction with heavy metals [3]. In studying this type of interaction, another electroanalytical method, conductometry, has already been proven to be a very useful tool [3]. Although its detection limit is insufficient for most environmental samples, conductometry is well suited for speciation purposes. Therefore the present study includes a treatment of the analysis of the conductivity of metal/polyelectrolyte systems.

VOLTAMMETRY

In voltammetry, the current at a working electrode is measured as a function of the applied potential. When a repeating mercury electrode is employed as a working electrode the term polarography is used to distinguish this special form of voltammetry. A typical current-potential relation is shown in Fig. 1. Under polarographic or stationary state conditions a wave-like voltammogram is usually obtained. The plateau corresponds to the limiting situation where the concentration of the electroactive analyte (i.e. the component to be determined) is zero at the electrode surface. The concentration gradient is at its maximum and the diffusion-controlled current takes a limiting value. In order to achieve this well-defined diffusion-controlled behaviour, efforts are made to avoid other forms of mass-transport of the analyte such as convection and conduction (or: migration). By avoiding vibration and stirring during the actual measurement, convection is practically eliminated. Conduction effects are normally minimized by introducing an excess of an electroinactive electrolyte. Therefore voltammetry is traditionally applied to systems with a low ratio between the concentration of the electroactive species and the inert electrolyte.

Under conditions of diffusion control the limiting current, I_ℓ, for a stationary planar electrode is given by the Cottrell equation which reads

$$I_\ell = nFAD^{\frac{1}{2}}c^*/(\pi t)^{\frac{1}{2}}$$

where n is the number of electrons involved in the electrode reaction, F the Faraday, A the surface area of the electrode, D and c^* are the diffusion coefficient and the bulk concentration of the analyte respectively and t is the time during which the elecrode potential is applied, i.e. the effective electrolysis time.

Another important characteristic of the current-potential relation is the half-wave potential, $E_{\frac{1}{2}}$. This is the potential at which the current is equal to half the limiting current. It permits qualitative identification of the analyte.

Voltammetry of complexes

Already in the early days of voltammetry, its potentialities for the study of metal complexes were recognized [4,5]. These systems consist in the simplest form of an electroactive metal ion (M) which associates with an electroinactive ligand (L) to form an electroinactive complex (ML)

$$M + L \underset{k_d}{\overset{k_a}{\rightleftarrows}} ML$$

where k_a and k_d are the association and dissociation rate constants respectively. Charges of ionic species are omitted for the sake of simplicity.

In a voltammetric experiment on the metal complex system, the consumption of M may be accompanied by dissociation of ML. Thus the comlpex may give rise to a net production of extra M which can be reduced. For this type of system the limiting current and the half-wave potential are at given experimental conditions governed by : (i) the homogeneous association/dissociation kinetics, i.e. the average life-times of M and ML, (ii) the diffusion coefficients of M and ML.

In the case of equal diffusion coefficients of M and ML, extensive theoretical treatments have been given by various authors for different electrode geometries [6,10]. In fact, until now the electrochemical literature almost exclusively dealt with this kind of systems [11,12]. However, in natural samples containing chelating agents such as fulvic and humic acids, the ligands are much larger than the uncomplexed metal and consequently their diffusion coefficient is significantly smaller. Although various authors carried out a lot of experimental work on the voltammetry of metal complex systems with large ligands such as fulvic and humic acids, proteins and synthetic polyacids [see ref. 3 for an extensive literature compilation], the importance of this aspect was only recently fully recognized [3,13,14]. In the last mentioned studies experimental data of labile complexes, that are complexes which give rise to a limiting current controlled by diffusion of ML, were analyzed using a tentative theoretical approach. In this respect the theoretical basis of voltammetry, which was advanced as one of the distinguished advantages [2] has been largely insufficient. The electrochemical literature on this subject only contains some tentative treatments [13,15] and some approximate theoretical studies [16,17] which suffer from quite severe limitations. Obviously, a rigorous treatment of the voltammetry of metal complex systems in which the diffusion coefficients of the species are different, is needed. The main part of the present study is concerned with the development of such a theory.

CONDUCTOMETRY

In conductometry the electrical resistance of an electrolyte solution is measured. The conductivity κ of a sample of an electrolyte may be defined in the same way as for a metallic conductor

$$\kappa = l/RA$$

where R is the resistance and l and A are the length and the surface area of the portion of the solution studied. For an electrolyte solution κ is related to the concentration c and the molar conductivity λ of the ions i.e.,

$$\kappa = \sum_i \lambda_i c_i$$

As was already indicated earlier, the conductometric assessment of heavy metal/polyelectrolyte interaction is of relevance for the analysis of environmental samples and has been the subject of many experimental and theoretical studies [18-26]. Theoretical treatments of the conductivity of polyelectrolyte solutions are generally based on the assumption that the ions are either in some kind of bound state or are completely free [25]. As a consequence of this assumption the conductivity of a polyelectrolyte solution may be formulated as

$$\kappa = \sum_i f_i \lambda_i c_i$$

where f_i is the fraction of ions of type i that are supposed to be completely free. The ions which are bound thus do not contribute to the overall conductivity of the solution.

In analyzing conductometric titrations of polyelectrolytes with solutions of multivalent metal nitrates, Cleven [3,27] employed a conductivity excess function, $\Delta\kappa_T$, defined by

$$\Delta\kappa_T = \Delta\kappa_b - \Delta\kappa_p$$

where $\Delta\kappa_b$ is the change of conductivity of a solution without polyelectrolyte, upon addition of the metal ions and $\Delta\kappa_p$ is the same for the solution with polyelectrolyte. The interpretation of data using this function remained more or less qualitative [3,27] especially because the role of the conductivity of the polyion was uncertain. For the further development of conductometric analysis a quantitative interpretation of the conductivity excess function is needed. In the present study such an interpretation is given. The role of the conductivity of the polyion has been assessed for systems in which the interaction between the counterions and the polyion is not specific. For such systems f_i is dependent only on the nature of the counterions, provided that they have the same charge. The molar conductivity of the polyion can then be evaluated from the relation between the overall molar conductivity of the polyelectrolyte solution and that of the counterions [24].

THE PRESENT STUDY

Purpose and overview of this study

The main purpose of this study is to develop the electroanalysis of the interaction of heavy metals with ligands which are much larger than the metal ions. The methods used here, voltammetry and conductometry, are to be applied in such a way that the physical chemical characteristics of the metal complex systems can be quantified experimentally. At least it should be possible to evaluate the equilibrium amounts of complexed and uncomplexed metal.

In the case of voltammetry this objective has led to the development of of a theory which gives a detailed description of the behaviour of the limiting current and the half-wave potential in metal complex systems with different diffusion coefficients of the species. This technique gives information about the stability constant of the complex and in certain cases also about the rate constant of the complex dissociation reaction.

For the conductometric analysis, the conductivity excess function is the cornerstone for the interpretation of the data. Using the two state approach advocated by Manning [20,28,29] this function is quantitatively described. In this way information is obtained about the fractions complexed and uncomplexed metal ions.

Model systems

The purpose of the present study is to develop appropriate theory for the electrochemical behaviour of metal/polyelectrolyte systems and to (re)consider the interpretation of experimental data. Suitable model systems should meet the following requirements:

i. the heavy metals should be polarographically active
ii. the ligand should have such dimensions that its diffusion coefficient differs substantially from that of the free metal.

As examples of the heavy metals Cd, Pb and Zn are chosen. They are

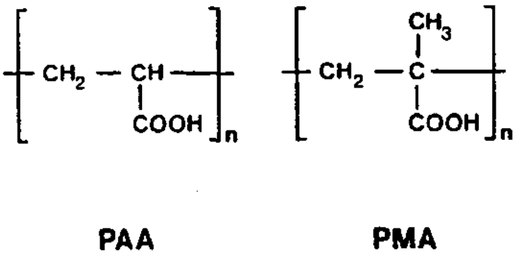

FIGURE 2 : Structural formulas of PAA and PMA.

polarographically active and of environmental relevance. Humic and fulvic acids are ligands occurring in nature, but they are not homogeneous with respect to thermodynamics and kinetics of metal binding and diffusion coefficient [30] and therefore they are not very suitable in the stage of verifying theory. A better choice is a homofunctional synthetic polyacid such as polyacrylicacid (PAA) or polymethacrylicacid (PMA). The structural formulas of these two macromolecules are shown in Fig.2. To a certain extent the stability constant of metal/polyelectrolyte complexes can be manipulated by adjusting the amount of negative charge on the polyion and this is a suitable feature in verifying theoretical elaborations. The physical chemistry of the association between metal ions and highly charged polymeric anions is still under development and many theoretical investigations are carried out on this subject [28,29,31-36]. In their interaction with heavy metals fulvic and humic acid exhibit polyelectrolyte-like behaviour [3] and metal ion association occurs predominantly through carboxylic groups [37,38]. It is clear that PAA and PMA share interesting and important properties with fulvic and humic acids and therefore are suitable choices with respect to both the environmental relevance and the methodological objectives of this work.

Outline of this thesis

In chapter 2 a rigorous theoretical treatment is given for the voltammetric limiting current of metal complex systems in which the diffusion coefficients of the species involved are different. The equation for the limiting current is formulated in the Laplace domain and is rigorous with respect to the values of the complex association and dissociation rate constants as well as to the values of the diffusion coefficient of the species. It is valid for an excess of ligand and a stationary planar electrode. In a number of limiting cases e.g. equal diffusion coefficients of the species, and very small values of the diffusion coefficient of the complex, analytical expressions in the time domain are derived.

Chapter 3 is concerned with the behaviour of the limiting current as a function of the electrolysis time, the ratio of the diffusion coefficients of the species and the association/dissociation rate constants. New qualifications to specify the behaviour of a metal complex are introduced. The lability concept is reformulated in an unambiguous and generalized manner. In order to facilitate practical use, some Cottrell plots and working curves are presented.

In chapter 4 the complete current-potential relation for voltammetry of metal complex systems is treated. The general relation is again formulated in the Laplace domain. Besides its limitation to reversible electrode processes, it has the same range of validity as the limiting current equation of chapter 2. The half-wave potential is obtained numerically from the general current-potential relation and its behaviour as a function of the electrolysis time, the ratio of the diffusion coefficients of the species and the association/-dissociation rate constants is discussed. In some special cases, analytical expressions for the half-wave potential in the time domain are derived.

In chapter 5 experimental data on the voltammetry of some heavy metal/-polyelectrolyte systems are (re)considered. The Zn/PMA system was found to be labile at the experimental time scale i.e. from 0.01 to 0.1 s electrolysis time. The stability constants calculated from limiting current and half-wave potential data agreed resonably well. The Pb/PAA system is not labile at the same time scale. In this case the equations from chapter 2, 3, and 4 were needed to estimate the stability constant.

In chapter 6 a procedure is described for the analysis of the conductivity of solutions of anionic polyelectrolytes in which both mono- and divalent counterions are present. Alkali polyacrylate solutions with and without alkali nitrate were titrated with zinc nitrate. The results give a picture of the counterionic atmosphere around the polyion. Up to a certain zinc/polyacid ratio the zinc ions are found to be bound quantitatively. The added zinc ions displace the bound alkali ions. The exchange ratio showed a discrete behaviour as a function of the zinc/polyacid ratio. For highly charged polyions this ratio is close to unity. The composition of the counterionic atmosphere is found to be largely independent of the alkali nitrate concentration.

REFERENCES

1. M. Waldichuk, in F.J. Vernberg and W.B. Vernberg (Eds.), Pollution and Physiology of Marine Organisms, Academic Press, New York, 1984.

2. H.W.Nürnberg, in W.F. Smyth (Ed.), Electroanalysis in Hygiene, Environmental, Clinical and Pharamceutical Chemistry, Analytical Symposia Series 2, Elsevier, Amsterdam, 1980.

3 R.M.F.J. Cleven, Ph.D. Thesis, Wageningen Agricultural University, Wageningen, 1984.

4. J. Heyrovský, D. Ilkovic, Collect. Czech. Chem. Commun.,7(1935)198.

5. J. Heyrovský, Polarographie, Springer, Wien, 1941.

6. H. Matsuda and, Y. Ayabe, Bull. Chem. Soc. Japan, 29(1956)134.

7. C. Nishihara and H. Matsuda, J.Electroanal.Chem., 51(1974)287.

8. H. Matsuda, J.Electroanal.Chem., 56(1974)165.

9. J. Galvez, A. Serna, A. Molina and D.Marin, J.Electroanal.Chem., 102(1979)277.

10. J. Galvez, C.Serna, A. Molina and A. Serna, J.Electroanal.Chem., 115(1980)1.

11. Z. Galus, Fundamentals of Electrochemical Analysis, Ellis Horwood, Chichester, 1976, Ch. 14.

12. D.R. Crow, Polarography of Metal Complexes, Academic Press, London, 1969.

13. R.M.F.J. Cleven, H.G. de Jong and H.P. van Leeuwen, J.Electroanal.Chem., 202(1986)57.

14. H.P. van Leeuwen, Sci. Tot. Environ., 60(1987)45.

15. R. Tamamushi and G.P. Sato, in P. Zuman (Ed.), Progress in Polarography, Vol. 3, Interscience, New York, 1972.

16. J. Koutecký, Collect.Czech.Chem.Commun., 19(1954)857.

17. M. Lovrić and I. Ružić, J.Electroanal.Chem., 146(1983)253.

18. J.R. Huizenga, Ph.F. Grieger, F.T. Wall, J.Am.Chem.Soc., 72(1950)2636.

19. H. Eisenberg, J.Polym.Sci., 30(1958).

20. G.S. Manning, Biopolymers, 9(1970)1543.

21. A. Schmitt and R. Varoqui, J.Chem.Soc., Faraday Trans. 2, 69(1973)1087.

22. J.C.T. Kwak, and R.C. Hayes, J.Phys.Chem., 79(1975)265.

23. G.S. Manning, J.Phys.Chem., 79(1975)262.

24. H. Vink, J.Chem.Soc., Faraday Trans. 1, 77(1981)2439.

25. D. Bratko, N. Celija, D. Dolar, J. Span, L. Trnkova and V. Vlachy, Makromol.Chem. Rapid Commun.,4(1983)783.

26. J.F. Thibault and M. Rinaudo, Biopolymers, 24(1985)2131.

27. R.M.F.J. Cleven and H.P. van Leeuwen, Intern. J. Environ. Anal. Chem., 27(1986)11.

28. G.S. Manning, J.Chem.Phys., 51(1969)924.

29. G.S. Manning, J.Chem.Phys., 51(1969)936.

30. M. Schnitzer and S.U. Kahn, Humic Substances in the Environment, Marcel Dekker, New York, 1976.

31. G.S. Manning, Quart. Rev. Biophys. 11(1978)179.

32. M. Guéron and G. Weisbuch, Biopolymers, 19(1980)353.

33. M. Guéron and G. Weisbuch, J.Phys.Chem., 85(1981)517.

34. B.H. Zimm and M. LeBret, J.Biomol.Struct.Dyn., 1(1983)461.

35. M. LeBret and B.H. Zimm, Biopolymers, 23(1984)271, 287.

36. P. Mills, C.F. Anderson and M.T. Record, J.Phys.Chem., 89(1985)3984.

37. P.Vinkler, B. Lakatos and J.Meisel, Geoderma 15(1976)231.

38. H. Kerndorff and M. Schnitzer, Geochim.Cosmochim Acta, 44(1980)1701.

J. Electroanal. Chem., 234 (1987) 1–16
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

CHAPTER 2

VOLTAMMETRY OF METAL COMPLEX SYSTEMS WITH DIFFERENT DIFFUSION COEFFICIENTS OF THE SPECIES INVOLVED

PART I. ANALYTICAL APPROACHES TO THE LIMITING CURRENT FOR THE GENERAL CASE INCLUDING ASSOCIATION/DISSOCIATION KINETICS

HANS G. DE JONG and HERMAN P. VAN LEEUWEN *

Laboratory for Physical and Colloid Chemistry, Agricultural University, De Dreijen 6,
6703 BC Wageningen (The Netherlands)

KAREL HOLUB

The J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences,
Jilská 16, 11000 Praha-1 (Czechoslovakia)

(Received 6th March 1987)

ABSTRACT

An exact solution is derived for the limiting current of a metal complex system for which the diffusion coefficients of the free and complexed metal are different. The solution is formulated in the Laplace domain and holds for a stationary planar electrode under conditions of an excess of ligand. It is valid for any set of values of the association/dissociation rate constants, which includes any value for the stability constant of the complex. In combination with a suitable inverse transformation method, highly interesting results are obtained for the current transients. The exactness of the treatment has been verified in various ways. For a number of limiting cases, fully analytical expressions in the time domain are derived. Important features appear, among them a generalized lability criterion for metal complex systems.

INTRODUCTION

The voltammetry of metal complexes has been a subject of considerable interest for many years. In the early days of polarography, the Czechoslovak school [1] drew attention to the specific potentialities of voltammetric techniques for the characterization of homogeneous complexation reactions of electroactive metal ions. Since then, much electrochemical work on metal complexes has been done (see, for

---

* To whom correspondence should be addressed.

example, ref. 2), practically all of it being devoted to complexes with diffusion coefficients equal to that of the uncomplexed metal. In theoretical treatments, the approximation of equal diffusion coefficients has always been very welcome since it leads to substantial simplification of the derivations of expressions for currents, for example. We are now facing the situation that practically all of the experimental polarographic experience and the theoretical background are applicable only to systems with small inorganic and organic ligands, where the diffusion coefficients of the different species are approximately equal.

In recent years, voltammetry has developed a high degree of popularity in the field of metal speciation in natural waters. Extensive lists of references to studies of heavy metal speciation in systems with large ligands such as humic acids, polysaccharides, polyelectrolytes, etc. can be given [3]. However, as indicated above, the theoretical basis for interpreting the experimental current data for these systems with strongly unequal diffusion coefficients is largely incomplete. Koutecký [4] derived an equation for the reduction current at a DME for the case of a (quasi-) monomolecular reaction scheme under the condition that the rate constants for the complex association/dissociation reactions are high with respect to the reciprocal time-scale of the experiment. Dogonadze's parallel treatment [5] for an RDE is limited by essentially the same kinetic prerequisites. Lovrić and Ružić [6] derived a current equation for the same type of reaction at a planar electrode, but their treatment is subject to the joint limitations of a large stability constant (practically all of the metal in complexed form) and not too different diffusion coefficients of the species.

There is an apparent need for a more general theory of the voltammetric behavior of metal complex systems with different diffusion coefficients of the species. Such a theory should be rigorous, at least with respect to the magnitudes of the diffusion coefficients and the rate constants of the complex association/dissociation reactions. We intend to outline in a series of papers that both analytical and numerical approaches can be applied successfully in achieving this goal. The present paper is devoted primarily to the analytical solutions that can be arrived at for the elementary system of an electroactive metal ion and an electroinactive complex for which (i) the diffusion coefficients are unequal, (ii) the rate constants of association/dissociation have finite values and (iii) the stability constant can have any value.

FORMULATION OF THE PROBLEM

In its most elementary form, a metal complex system consists of a metal ion M which may be reduced to the metal $M^{\cdot}$, and a ligand L with which M may form the electroinactive complex ML:

$$\begin{array}{l} \mathrm{M} \quad + \mathrm{L} \underset{k_d}{\overset{k_a}{\rightleftarrows}} \mathrm{ML} \\ \uparrow\downarrow n\,e^- \\ \mathrm{M}^{\cdot} \end{array} \tag{1}$$

Charges of ionic species are omitted for the sake of simplicity. The rate constants k_a and k_d determine the stability constant K of the complex:

$$K = k_a/k_d \tag{2}$$

For semi-infinite diffusion of M, L and ML to or from a stationary planar electrode, we may write

$$\frac{\partial c_M}{\partial t} = D_M \frac{\partial^2 c_M}{\partial x^2} + k_d(c_{ML} - K c_M c_L) \tag{3a}$$

$$\frac{\partial c_L}{\partial t} = D_L \frac{\partial^2 c_L}{\partial x^2} + k_d(c_{ML} - K c_M c_L) \tag{3b}$$

$$\frac{\partial c_{ML}}{\partial t} = D_{ML} \frac{\partial^2 c_{ML}}{\partial x^2} - k_d(c_{ML} - K c_M c_L) \tag{3c}$$

with the boundary conditions

$$\begin{array}{lll} t = 0, & x \geqslant 0 & c_{ML}/c_M c_L = K \\ t > 0, & x \rightarrow \infty & c_M = c_M^*, \quad c_L = c_L^*, \quad c_{ML} = c_{ML}^* \end{array} \tag{4}$$

where c and c^* denote the concentration and bulk concentration, respectively. In the limiting current regime, further boundary conditions for the system under consideration are

$$t > 0, \quad x = 0 \quad \begin{cases} c_M = 0 & \text{(5a)} \\ \partial c_{ML}/\partial x, \quad \partial c_L/\partial x = 0 & \text{(5b)} \end{cases}$$

Here, we will restrict ourselves to the case of an excess of ligand L, i.e. $c_L^* \gg (c_M^* + c_{ML}^*)$, so that the complex association reaction becomes quasi-monomolecular. Then one is allowed to replace the constants k_a and K by

$$k_a' = k_a c_L^* \tag{6a}$$

$$K' = K c_L^* = c_{ML}^*/c_M^* \tag{6b}$$

and the transport of L, eqn. (3b), can be ignored.

Under the conditions given and after transformation into the Laplace domain, the transport equations (3a) and (3c) read

$$\frac{d^2 \bar{c}_M}{dx^2} = \frac{s + k_a'}{D_M} \bar{c}_M - \frac{k_d}{D_M} \bar{c}_{ML} - \frac{c_M^*}{D_M} \tag{7a}$$

$$\frac{d^2 \bar{c}_{ML}}{dx^2} = -\frac{k_a'}{D_{ML}} \bar{c}_M + \frac{s + k_d}{D_{ML}} \bar{c}_{ML} - \frac{c_{ML}^*}{D_{ML}} \tag{7b}$$

where s is the Laplace transform parameter and the overbar denotes a transformed variable.

RIGOROUS SOLUTION

The set of simultaneous differential equations (7a) and (7b) can be treated according to d'Alembert's method. This involves the selection of a new set of equations for a variable which is a linear combination of the original variables $\bar{c}_{\mathrm{M}}$ and $\bar{c}_{\mathrm{ML}}$. For this purpose, we define

$$\Psi_{\pm} \equiv \bar{c}_{\mathrm{ML}} \pm k_{\pm} \bar{c}_{\mathrm{M}} \tag{8}$$

and choose $k_{\pm}$ to be (see Appendix A for a brief explanation)

$$k_{\pm} = d_{-} \pm d_{\mathrm{r}} \tag{9}$$

with

$$d_{\pm} = \tfrac{1}{2}\left[\frac{s}{k_{\mathrm{d}}}(\epsilon^{-1} \pm 1) + \epsilon^{-1} \pm K'\right] \tag{10}$$

$$d_{\mathrm{r}} = \left(d_{-}^{2} + K'\epsilon^{-1}\right)^{1/2} \tag{11}$$

where

$$\epsilon = D_{\mathrm{ML}}/D_{\mathrm{M}} \tag{12}$$

Following d'Alembert's methodology, eqns. (7a) and (7b) are replaced by

$$\frac{\mathrm{d}^2\Psi_{\pm}}{\mathrm{d}x^2} = \left(\frac{s + k_{\mathrm{d}}}{D_{\mathrm{ML}}} - \frac{k_{\pm}k_{\mathrm{d}}}{D_{\mathrm{M}}}\right)\Psi_{\pm} - \left(\frac{c_{\mathrm{ML}}^{*}}{D_{\mathrm{ML}}} + \frac{k_{\pm}c_{\mathrm{M}}^{*}}{D_{\mathrm{M}}}\right) \tag{13}$$

which may be solved straightforwardly to give

$$\Psi_{\pm} = \frac{c_{\mathrm{ML}}^{*} + k_{\pm}\epsilon c_{\mathrm{M}}^{*}}{s + k_{\mathrm{d}} - k_{\pm}k_{\mathrm{d}}\epsilon} + A_{\pm}(s)\exp\left[-\left(\frac{s + k_{\mathrm{d}}}{D_{\mathrm{ML}}} - \frac{k_{\pm}k_{\mathrm{d}}}{D_{\mathrm{M}}}\right)^{1/2} x\right] \tag{14}$$

The integration constants $A_{+}(s)$ and $A_{-}(s)$ can be found by exploiting the boundary conditions (5a) and (5b). Reformulated for $\Psi_{\pm}$, these conditions are

$$x = 0 \quad \begin{cases} \Psi_{+} - \Psi_{-} = 0 & \text{(15a)} \\ -\dfrac{k_{-}}{k_{+} - k_{-}}\dfrac{\mathrm{d}\Psi_{+}}{\mathrm{d}x} + \dfrac{k_{+}}{k_{+} - k_{-}}\dfrac{\mathrm{d}\Psi_{-}}{\mathrm{d}x} = 0 & \text{(15b)} \end{cases}$$

and their application to eqn. (14) leads to

$$A_{-}(s) = \frac{c_{\mathrm{M}}^{*}}{k_{\mathrm{d}}}\,\frac{\left(d_{-} + d_{\mathrm{r}} + K'\epsilon^{-1}\right) - \left(d_{-} - d_{\mathrm{r}} + K'\epsilon^{-1}\right)(d_{+} - d_{\mathrm{r}})(d_{+} + d_{\mathrm{r}})^{-1}}{(d_{+} - d_{\mathrm{r}}) - (d_{-} + d_{\mathrm{r}})(d_{-} - d_{\mathrm{r}})^{-1}\left(d_{+}^{2} - d_{\mathrm{r}}^{2}\right)^{1/2}} \tag{16a}$$

$$A_{+}(s) = \frac{c_{\mathrm{M}}^{*}}{k_{\mathrm{d}}}\left[\frac{d_{-} - d_{\mathrm{r}} + K'\epsilon^{-1}}{d_{+} + d_{\mathrm{r}}} - \frac{d_{-} + d_{\mathrm{r}} + K'\epsilon^{-1}}{d_{+} - d_{\mathrm{r}}}\right] + A_{-}(s) \tag{16b}$$

From the profiles of Ψ_+ and Ψ_- the gradient $(\mathrm{d}\bar{c}_\mathrm{M}/\mathrm{d}x)_{x=0}$ can be obtained by using, for example,

$$\left(\frac{\mathrm{d}\bar{c}_\mathrm{M}}{\mathrm{d}x}\right)_{x=0} = \frac{1}{k_-}\left(\frac{\mathrm{d}\Psi_-}{\mathrm{d}x}\right)_{x=0} \tag{17}$$

resulting in

$$\begin{aligned}\left(\frac{\mathrm{d}\bar{c}_\mathrm{M}}{\mathrm{d}x}\right)_{x=0}& \\ = -&\frac{c_\mathrm{M}^*}{D_\mathrm{M}^{1/2}k_\mathrm{d}^{1/2}} \\ &\times \frac{\left(d_+ + d_\mathrm{r} + K'\epsilon^{-1}\right)\left(d_+ + d_\mathrm{r}\right)^{1/2} - \left(d_- - d_\mathrm{r} + K'\epsilon^{-1}\right)\left(d_+ - d_\mathrm{r}\right)\left(d_+ + d_\mathrm{r}\right)^{-1/2}}{\left(d_+ - d_\mathrm{r}\right)\left(d_- - d_\mathrm{r}\right) - \left(d_- + d_\mathrm{r}\right)\left(d_+^2 - d_\mathrm{r}^2\right)^{1/2}}\end{aligned} \tag{18}$$

To some extent, this equation can be rearranged in order to make it more explicit in s:

$$\left(\frac{\mathrm{d}\bar{c}_\mathrm{M}}{\mathrm{d}x}\right)_{x=0} = +\frac{2c_\mathrm{M}^*k_\mathrm{d}^{1/2}}{D_\mathrm{ML}^{1/2}}\frac{(s+l)^{1/2}(d_- + d_\mathrm{r})(d_+ + d_\mathrm{r})^{1/2}d_\mathrm{r}}{\left[K'\epsilon^{-3/2}s^{1/2}(s+l)^{1/2} + k_\mathrm{d}(d_- + d_\mathrm{r})^2(d_+ + d_\mathrm{r})\right]s^{1/2}} \tag{19}$$

where

$$l \equiv k_\mathrm{d}(1+K') = k_\mathrm{a}' + k_\mathrm{d} \tag{20}$$

Equation (19) is too complicated to allow analytical inversion to the original transient. Later we will see that this is possible only in a number of limiting cases. The inversion of eqn. (18) or (19) to the time domain can be carried out numerically, using the computation method developed by Crump [7]. The procedure involves an approximation of the general inversion formula

$$f(t) = \frac{\exp(at)}{\pi}\int_0^\infty \left[\mathrm{Re}\{\bar{f}(s)\}\cos\omega t - \mathrm{Im}\{\bar{f}(s)\}\sin\omega t\right]\mathrm{d}\omega \tag{21}$$

by a Fourier series containing both cosine and sine terms, selected such that the error is minimized:

$$\begin{aligned}f(t) = \frac{\exp(at)}{T}&\left[\tfrac{1}{2}\bar{f}(a) + \sum_{k=1}^{\infty}\left[\mathrm{Re}\{\bar{f}(a+k\pi\mathrm{i}/T)\}\cos(k\pi t/T)\right.\right. \\ &\left.\left. - \mathrm{Im}\{\bar{f}(a+k\pi\mathrm{i}/T)\}\sin(k\pi t/T)\right]\right] - \text{error}\end{aligned} \tag{22}$$

where T is some number greater than $t/2$, a is some number greater than the exponential order of $f(t)$ and the error is given by

$$\text{error} = \sum_{n=1}^{\infty} \exp(-2naT) f(2nT+t) \tag{23}$$

In conjunction with this series approximation procedure, the rate of convergence is increased by applying the epsilon algorithm series transformation [7]. The complete inversion program is available as a FORTRAN subroutine (FLINV) in the IMSL Library [8]. We tested the program on a DEC VAX 8600 computer with a number of transients of the type $t^{-1/2}$ and experfc $(t^{1/2})$. The result was that the inversions, exact up to five digits over the complete decay function, could be performed within a few seconds CPU time and this is most satisfactory.

The inversion of eqn. (18) according to the procedure given was without any problem. A typical example of some results is given in Fig. 1, where the calculated normalized current Φ is given as a function of the normalized time $(k_a't)$ for a given set of parameter values. The current parameter Φ is defined as

$$\Phi = \frac{(\pi D_M t)^{1/2}}{c_T^*} L^{-1}\{(\mathrm{d}\bar{c}_M/\mathrm{d}x)_{x=0}\} \tag{24}$$

where $c_T^* = c_M^* + c_{ML}^*$ and L^{-1} denotes the inverse transform. Φ thus represents the current as compared with the current under the condition that all the metal is present as the free metal species M, with a diffusion coefficient D_M. As long as D_{ML} is smaller than D_M, which is the usual situation, Φ is between zero and unity. The results in Fig. 1, as well as other properties of the current for the present system, will be discussed extensively in a separate paper [9]. Here, we just want to

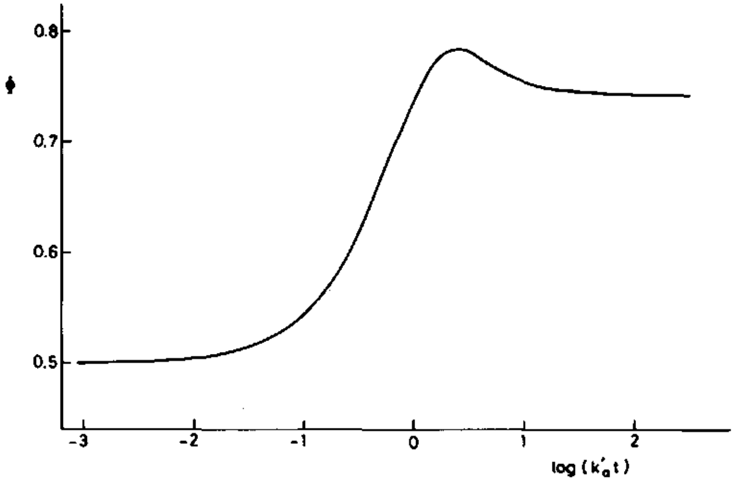

Fig. 1. The normalized current Φ as a function of the normalized time $k_a't$, as obtained from eqn. (18). ϵ $(=D_{ML}/D_M)=0.1$; $K'=1$.

TABLE 1

Calculated transients (Φ, t): (a) from digital simulation [11], using different step sizes; (b) from inversion of eqn. (18). $\epsilon = 0.1$, $K' = 1$, $k_d = 1\ s^{-1}$

t/s	(a) 1000 steps	(a) 10000 steps	(a) 100000 steps	(b)
0.01	0.504258	0.504849	0.504939	0.504963
0.125	0.553928	0.555899	0.556440	0.556676
0.25	0.598575	0.601735	0.602662	0.603078
0.5	0.665074	0.669860	0.671309	0.671969
1	0.738612	0.744719	0.746569	0.747411
2	0.780574	0.786205	0.787826	0.788549
4	0.774726	0.778110	0.778926	0.779261
8	0.757113	0.758944	0.759259	0.759360
16	0.748004	0.749384	0.749576	0.749625
32	0.744010	0.745243	0.745398	0.745432
64	0.742153	0.743320	0.743457	0.743342
128	0.741259	0.742394	0.742520	0.742542

establish its correctness as a rigorous solution for the metal complex system under the above-mentioned conditions.

It is easily verified from Fig. 1 that the short-time limit corresponds to the response for the free metal only, i.e. to the region where the complex is inert. In the long-time limit, the response corresponds to the mean diffusion coefficient of the complex system as has already been predicted for these conditions [10]. As a final test, we calculated the Φ, t curve directly from the original differential equations, using the explicit finite difference methodology of Feldberg [11]. Although this is probably not the most suitable numerical technique for the present problem, we used it at this stage because it is easy to program and sufficient for the purpose of verifying eqn. (18). A comprehensive evaluation of the application of different numerical techniques to the present system will be the subject of an intended separate investigation. Table 1 shows some results of the comparison between the inversion of eqn. (18) and the numerical simulation. The agreement is quite reasonable, provided that the step size in the simulation is sufficiently small. Anyway, the time steps must be smaller than $1/k'_a$ and $1/k_d$, otherwise the simulation does not work. It is interesting to note here a few further aspects: (i) with decreasing step size, the digital simulation yields results that are closer and closer to the results from the Laplace domain formula (18); (ii) for some limiting cases (to be discussed below), the agreement between the exact solution for the transient and the numerical inversion of eqn. (18) is perfect; (iii) the computation of the inverse of eqn. (18) is several orders of magnitude faster than the digital simulation procedure; even for not too severe accuracy requirements and not too high $k'_a t$ and $k_d t$ values, the computing times typically differ by a factor of 10^3. Summarizing the results, it can be concluded that the newly derived equation for the gradient, eqn. (18) or (19), is an exact expression. In combination with a suitable inversion algorithm, it provides us with a fundamental extension of the voltammetry of metal complex systems.

SOME LIMITING CASES

Starting from the general expression for the gradient, eqn. (18) or (19), or at some stage of its derivation, it is possible to impose simplifying conditions which allow the formulation of analytical expressions for the transient in the time domain.

(A) $D_{ML}/D_M \rightarrow 0$

Under conditions where the diffusion of the complex species ML may be neglected, the starting differential equation for ML, eqn. (3c), loses the term with D_{ML}. Then eqn. (7b) is simplified to

$$-k'_{\mathrm{a}}\bar{c}_{\mathrm{M}} + (s + k_{\mathrm{d}})\bar{c}_{\mathrm{ML}} - c^*_{\mathrm{ML}} = 0 \tag{25}$$

and this allows direct substitution of $\bar{c}_{\mathrm{ML}}$ into eqn. (7a), yielding

$$\frac{\mathrm{d}^2\bar{c}_{\mathrm{M}}}{\mathrm{d}x^2} = \frac{1}{D_{\mathrm{M}}}\left[\frac{s(s+l)}{s+k_{\mathrm{d}}}\right]\bar{c}_{\mathrm{M}} - \frac{c^*_{\mathrm{M}}}{D_{\mathrm{M}}}\left[\frac{s+l}{s+k_{\mathrm{d}}}\right] \tag{26}$$

Taking into account the boundary conditions (5), this can be solved to

$$\bar{c}_{\mathrm{M}} = \frac{c^*_{\mathrm{M}}}{s}\left[1 - \exp\left(-\frac{s^{1/2}(s+l)^{1/2}}{D_{\mathrm{M}}^{1/2}(s+k_{\mathrm{d}})^{1/2}}x\right)\right] \tag{27}$$

yielding for the gradient at the electrode surface

$$\left(\frac{\mathrm{d}\bar{c}_{\mathrm{M}}}{\mathrm{d}x}\right)_{x=0} = \frac{c^*_{\mathrm{M}}}{D_{\mathrm{M}}^{1/2}}\frac{(s+l)^{1/2}}{s^{1/2}(s+k_{\mathrm{d}})^{1/2}} \tag{28}$$

For the case where D_{ML} is finite but still very much smaller than D_{M} ($\epsilon = D_{\mathrm{ML}}/D_{\mathrm{M}} \ll 1$), it is possible to approach the problem by writing the concentration functions in asymptotic sequences:

$$\left.\begin{aligned} c_{\mathrm{M}} &= c_{\mathrm{M},0} + \epsilon c_{\mathrm{M},1} + \epsilon^2 c_{\mathrm{M},2} + \cdots \\ c_{\mathrm{ML}} &= c_{\mathrm{ML},0} + \epsilon c_{\mathrm{ML},1} + \epsilon^2 c_{\mathrm{ML},2} + \cdots \end{aligned}\right\} \tag{29}$$

Substitution of eqns. (29) into the differential eqns. (3a) and (3c) and equating terms of like powers in ϵ generates a new set of differential equations. In this set, the zero-order equation ($\epsilon = 0$) is identical to eqn. (26) and the further terms are given by

$$\left.\begin{aligned} \frac{\partial c_{\mathrm{M},i}}{\partial\tau} &= \frac{\partial^2 c_{\mathrm{M},i}}{\partial\eta^2} + \lambda(c_{\mathrm{ML},i} - K'c_{\mathrm{M},i}) \\ \frac{\partial c_{\mathrm{ML},i}}{\partial\tau} &= \epsilon^i\frac{\partial^2 c_{\mathrm{ML},i-1}}{\partial\eta^2} - \lambda(c_{\mathrm{ML},i} - K'c_{\mathrm{M},i}) \end{aligned}\right\} \quad i = 1, 2, \ldots \tag{30}$$

where

$$\tau = (k_a' + k_d)t \tag{31}$$

$$\eta = \left(\frac{k_a' + k_d}{D_M}\right)^{1/2} x \tag{32}$$

$$\lambda = (1 + K')^{-1} \tag{33}$$

The boundary conditions for eqn. (30) run parallel with those in eqns. (4) and (5). For the first-order approximation, taking the terms with ϵ^1 into account, it follows that

$$\bar{c}_M = \frac{c_M^*}{s}\left[1 - \left(1 - \frac{\epsilon K' l^{3/2} s^{1/2}(s+l)^{1/2}}{2(1+K')^2(s+k_d)^{5/2}}\eta\right)\exp\left(-\frac{s^{1/2}(s+l)^{1/2}}{l^{1/2}(s+k_d)^{1/2}}\eta\right)\right] \tag{34}$$

from which

$$\left(\frac{d\bar{c}_M}{dx}\right)_{x=0} = \frac{c_M^*}{D_M^{1/2}}\left[\frac{(s+l)^{1/2}}{s^{1/2}(s+k_d)^{1/2}} + \frac{\epsilon K' l^2 (s+l)^{1/2}}{2(1+K')^2 s^{1/2}(s+k_d)^{5/2}}\right] \tag{35}$$

For expression (35) it is possible to carry out the inverse transformation into the time domain. Details are given in Appendix B. The result is

$$\Phi(t) = \frac{\pi^{1/2}}{(1+K')}\left\{\Psi_0(k_\alpha'; k_d; t) + \frac{\epsilon K'}{2(1+K')^2}\Psi_2(k_a'; k_d; t)\right\} \tag{36}$$

where

$$\begin{aligned}
&\Psi_m(k_a'; k_d; t)\\
&\quad = \frac{(lt)^m}{\Gamma(m+\frac{1}{2})}\exp(-k_d t) + \tfrac{1}{2}\exp\left(-\frac{1}{2}lt\right)\sum_{j=0}^{\infty}\frac{\Gamma(2j+1)(lt)^{2j+m+1}}{\Gamma(2j+m+3/2)4^{2j}(j!)^2}\\
&\quad \times\Big\{{}_1F_1\left(m+\tfrac{1}{2};\, 2j+m+3/2;\, \tfrac{1}{2}(k_a'-k_d)t\right)\\
&\quad + \frac{(2j+1)lt}{4(2j+m+3/2)(j+1)}\,{}_1F_1\left(m+\tfrac{1}{2};\, 2j+m+5/2;\, \tfrac{1}{2}(k_a'-k_d)t\right)\Big\}
\end{aligned} \tag{37}$$

in which Γ is the gamma function and ${}_1F_1$ is the hypergeometric Kummers function, defined by

$${}_1F_1(a;\, b;\, z) = 1 + \frac{a}{b}z + \frac{a(a+1)}{b(b+1)}\frac{z^2}{2!} + \frac{a(a+1)(a+2)}{b(b+1)(b+2)}\frac{z^3}{3!} + \cdots \tag{38}$$

The correctness and usefulness of expression (37) can be read from Table 2, where some calculated transients for different ϵ are compared with the results from the inversion of the exact eqn. (18). As expected, the agreement is very good for low ϵ, whereas it is readily lost at higher ϵ, especially if lt is not much smaller than unity.

TABLE 2

Calculated transient (Φ, t) for different values of $\epsilon(D_{\mathrm{ML}}/D_{\mathrm{M}})$: (a) from inversion of eqn. (18); (b) from eqn. (37). $K'=10$, $k_{\mathrm{d}}=1\ \mathrm{s}^{-1}$

t/s	$\epsilon=10^{-4}$		$\epsilon=10^{-2}$		$\epsilon=10^{-1}$	
	(a)	(b)	(a)	(b)	(a)	(b)
0.01	0.099793	0.099792	0.099793	0.099793	0.099796	0.099798
0.125	0.178437	0.178436	0.178521	0.178541	0.178992	0.179488
0.25	0.232361	0.232360	0.232701	0.232798	0.234535	0.236778
0.5	0.292911	0.292911	0.294232	0.294679	0.300883	0.310753
1	0.338747	0.338749	0.343171	0.344932	0.363793	0.401134
2	0.347672	0.347676	0.358587	0.363214	0.407618	0.504469
4	0.327675	0.327679	0.344481	0.349813	0.426753	0.551032
8	0.312109	0.312109	0.329027	0.330878	0.430295	0.501507
16	0.306320	0.306321	0.321977	0.322643	0.429259	0.471023
32	0.303893	0.303893	0.318928	0.319443	0.428020	0.460809
64	0.302565	0.302756	0.317396	0.317979	0.427252	0.456374
128	0.302425		0.317133		0.427119	accuracy lost

(B) $D_{ML}/D_M \rightarrow 1$

For the degenerate case where $D_{\mathrm{ML}} = D_{\mathrm{M}} = D$, we have:

$$\epsilon = 1 \qquad d_+ = \frac{1}{k_{\mathrm{d}}}\left(s + \tfrac{1}{2}l\right)$$

$$d_- = \tfrac{1}{2}(1 - K') \qquad d_r = \tfrac{1}{2}(1 + K')$$

so that eqn. (19) is simplified to

$$\left(\frac{\mathrm{d}\bar{c}_{\mathrm{M}}}{\mathrm{d}x}\right)_{x=0} = \frac{(1+K')c_{\mathrm{M}}^*}{D^{1/2}}\,\frac{(s+l)^{1/2}}{s^{1/2}\left[K's^{1/2} + (s+l)^{1/2}\right]} \tag{39}$$

This expression is identical to the result obtained by Koutecký and Brdička [12]. After some rearrangement, the analytical solution for the transient, valid for both $K' > 1$ and $K' < 1$, is found as (see Appendix C for details):

$$\begin{aligned}\Phi(t) = \frac{(\pi t)^{1/2}}{(K'^2-1)}\Bigg\{ & K'\exp\left(\frac{l+l'}{2}t\right)\sum_{j=1}^{\infty}\frac{\left[\frac{1}{4}(l+l')\right]^{2j}\Gamma(2j+1)t^{2j-1/2}}{\Gamma(2j+\frac{1}{2})(j!)^2}\\ & \times\left[\left\{1+\frac{(l+l')t}{2(2j+\frac{1}{2})}\right\}{}_1F_1\left(\tfrac{1}{2};\,2j+3/2;\,\frac{l+l'}{2}t\right)\right.\\ & \left.+\frac{(l+l')t}{4(2j+5/2)(2j+3/2)}\,{}_1F_1\left(\tfrac{1}{2};\,2j+5/2;\,\frac{l+l'}{2}t\right)\right]\\ & -\frac{1}{\pi^{1/2}}\left[\left(\frac{1}{t^{1/2}}+2lt^{1/2}\right){}_1F_1(1;\,3/2;\,l't)\right.\\ & \left.\left.+\frac{4l't^{1/2}}{3}\,{}_1F_1(2;\,5/2;\,l't)\right]\right\}\end{aligned} \tag{40}$$

TABLE 3

Calculated transient (Φ, t) for $\epsilon = 1$ and different k_d values: (a) from inversion of eqn. (18): (b) from eqn. (40). $K' = 10$

t/s	$k_d = 10^{-1}$ s^{-1}		$k_d = 1$ s^{-1}	
	(a)	(b)	(a)	(b)
0.01	0.091817	0.091816	0.099808	0.099807
0.125	0.101974	0.101973	0.180618	0.180616
0.25	0.112471	0.112471	0.240337	0.240335
0.5	0.131940	0.131940	0.319546	0.319544
1	0.165779	0.165778	0.414963	0.414961
2	0.218861	0.218860	0.522158	0.522157
4	0.292096	0.292106	0.633575	0.633574
8	0.382759	0.382698	0.738900	0.738898
16	0.486751	0.486750	0.828110	0.828107
32	0.597845	0.597844	0.895265	0.895259
64	0.706319	0.706317	0.940330	0.940017
128	0.801628	0.801626	0.967703	accuracy lost

where

$$l' = l/(K'^2 - 1) \tag{41}$$

Since expression (40) is still rather involved, we tested it by making some calculations and comparing these with the results from the rigorous eqn. (18). As can be seen from Table 3, the agreement is excellent. For high values of lt, the computation of eqn. (40) loses accuracy because the precision requirements for evaluating the series involved become too severe.

Returning to eqn. (39), it is readily seen that further simplification leads to sound limits. For $K' \to 0$, i.e. when there is practically no complex, the gradient becomes $c_M^*(Ds)^{1/2}$, which corresponds to the normal Cottrell response of the free metal M. For $l/s \to 0$, i.e. when the conversion of ML into M and vice versa is very slow, the result for the gradient is again $c_M^*/(Ds)^{1/2}$, reflecting that only diffusion of the free metal is responsible for the current.

(C) The short time limit ($s \to \infty$)

If s satisfies the conditions

$$\frac{s}{k_d}, \frac{s}{k'_a} \gg 1 \tag{42}$$

then $d_\pm$ is simplified to $\frac{1}{2}(\epsilon^{-1} \pm 1)s/k_d$ and eqn. (19) is reduced to

$$\left(\frac{d\bar{c}_M}{dx}\right)_{x=0} = \frac{c_M^*}{D_M^{1/2}} \frac{(s+l)^{1/2}}{s} \tag{43}$$

Since $s \gg l$, which is already implied by condition (42), we obtain for the gradient $c_M^*/(D_M s)^{1/2}$. As in the previous section, this is again the diffusional response of M only. The conditions imply that the complex ML does not contribute to the current in this regime, where Φ is simply $c_{\mathrm{M}}^{*}/c_{\mathrm{T}}^{*}$.

(D) The long time limit ($s \to 0$)

If s is so small that

$$\frac{s}{k_{\mathrm{d}}},\ \frac{s}{k_{\mathrm{a}}'} \ll 1 \tag{44}$$

then $d_{\pm}$ reduces to $\frac{1}{2}(\epsilon^{-1} \pm K')$ and eqn. (19) is simplified to

$$\left(\frac{\mathrm{d}\bar{c}_{\mathrm{M}}}{\mathrm{d}x}\right)_{x=0} = \frac{c_{\mathrm{M}}^{*} k_{\mathrm{d}}^{1/2}}{D_{\mathrm{ML}}^{1/2}} \frac{l^{1/2}(\epsilon^{-1} + K')^{3/2}}{\left[K'\epsilon^{-1/2}s^{1/2}l^{1/2} + k_{\mathrm{d}}\epsilon^{-1}(\epsilon^{-1} + K')\right]s^{1/2}} \tag{45}$$

The first term in brackets in the denominator of eqn. (45) may be neglected if s satisfies a further condition:

$$s \ll \frac{k_{\mathrm{d}}^{2}}{(k_{\mathrm{a}}' + k_{\mathrm{d}})}\epsilon^{-1}\left(\frac{\epsilon^{-1}}{K'} + 1\right)^{2} \tag{46}$$

It will be outlined [9] that condition (46) is, in fact, a generalized form of the electrochemical lability criterion for a metal complex system. With this condition satisfied, the expression for the gradient reduces to

$$\left(\frac{\mathrm{d}\bar{c}_{\mathrm{M}}}{\mathrm{d}x}\right)_{x=0} = \frac{c_{\mathrm{M}}^{*}}{D_{\mathrm{M}}^{1/2}s^{1/2}}(1 + K')^{1/2}(1 + \epsilon K')^{1/2} \tag{47}$$

Recalling that the mean diffusion coefficient $\overline{D}$ for the present system is given by

$$\overline{D} = \frac{c_{\mathrm{ML}}^{*}}{c_{\mathrm{T}}^{*}} D_{\mathrm{ML}} + \frac{c_{\mathrm{M}}^{*}}{c_{\mathrm{T}}^{*}} D_{\mathrm{M}} \tag{48}$$

eqn. (47) can be rewritten as

$$\left(\frac{\mathrm{d}\bar{c}_{\mathrm{M}}}{\mathrm{d}x}\right)_{x=0} = \frac{c_{\mathrm{T}}^{*}\overline{D}^{1/2}}{D_{\mathrm{M}}s^{1/2}} \tag{49}$$

which is identical to the result obtained by Koutecký [4]. The appearance of the mean diffusion coefficient in this specific limiting case is a further illustration of the general validity of eqn. (19). Some interesting features of the "dynamic" regime will be discussed in detail elsewhere [9].

APPENDIX A

d'Alembert's method for treating simultaneous differential equations

Consider the two differential equations

$$\frac{\mathrm{d}f}{\mathrm{d}u} = af + bg + c \tag{A1}$$

$$\frac{\mathrm{d}g}{\mathrm{d}u} = a'f + b'g + c' \tag{A2}$$

from which, by linear combination, the following equation can be written:

$$\frac{\mathrm{d}(f+mg)}{\mathrm{d}u} = (a+ma')f + (b+mb')g + (c+mc') \tag{A3}$$

Equation (A3) can be formulated in terms of one new variable if the constant m is selected such that $(b+mb') = m(a+ma')$, i.e. if m is equalized to the roots $(m_{\pm})$ of the quadratic equation

$$m^2 + \frac{(a-b')}{a'}m - \frac{b}{a'} = 0 \tag{A4}$$

The original differential equations of the variables f and g may now be replaced by the new pair of equations of one variable, $(f+m_{+}g)$ or $(f+m_{-}g)$:

$$\frac{\mathrm{d}(f+m_{\pm}g)}{\mathrm{d}u} = (a+m_{\pm}a')(f+m_{\pm}g) + (c+m_{\pm}c') \tag{A5}$$

APPENDIX B

Inverse Laplace transformation of eqn. (35)

The basic element, denoted as G_m, in the inversion of eqn. (35) is

$$G_m(s) = \frac{(s+l)^{1/2}}{s^{1/2}(s+k_\mathrm{d})^{m+1/2}} \quad \text{with } m = 0 \text{ or } 2 \tag{B1}$$

This expression can be rearranged to

$$G_m(s) = \frac{1}{(s+k_\mathrm{d})^{m+1/2}} + \frac{1}{(s+k_\mathrm{d})^{m+1/2}}\left\{\frac{(s+l)^{1/2}}{s^{1/2}} - 1\right\} \tag{B2}$$

Using the convolution theorem, the inversion yields

$$G_m(t) = \frac{t^{m-1/2}}{\Gamma(m+\frac{1}{2})}\exp(-k_\mathrm{d}t) + \frac{l\exp(-k_\mathrm{d}t)}{2\Gamma(m+\frac{1}{2})} \times \int_0^t (t-u)^{m-1/2}\exp\left[-\tfrac{1}{2}(k_\mathrm{a}'-k_\mathrm{d})u\right]\left[I_0(\tfrac{1}{2}lu) + I_1(\tfrac{1}{2}lu)\right]\mathrm{d}u \tag{B3}$$

where I_0 and I_1 are modified Bessel functions of the zeroth and first order, respectively. These functions may be expanded in series [13]:

$$I_\nu(z) = (\tfrac{1}{2}z)^\nu \sum_{j=0}^{\infty} \frac{(\frac{1}{4}z)^{2j}}{j!\Gamma(\nu+j+1)} \tag{B4}$$

Substitution into eqn. (B3) yields an expression that can be integrated term-by-term using the formula [14]

$$\int_0^t [t-u]^{\mu-1}u^{\alpha-1}\exp(\beta u)\,\mathrm{d}u = B(\mu,\alpha)t^{\alpha+\mu-1}\,{}_1F_1(\alpha;\alpha+\mu;\beta t) \tag{B5}$$

where B is the beta function and ${}_1F_1$ is Kummers' confluent hypergeometric function.

APPENDIX C

Inverse Laplace transformation of eqn. (39)

Written in the form of the normalized gradient Φ, eqn. (39) reads

$$\Phi(t) = (\pi t)^{1/2} L^{-1}\left\{ \frac{(s+l)^{1/2}}{s^{1/2}\left[K' s^{1/2} + (s+l)^{1/2}\right]} \right\} \tag{C1}$$

which can be rearranged to

$$\Phi(t) = \frac{(\pi t)^{1/2}}{K'^2 - 1}\left[K' L^{-1}\left\{ \frac{s}{(s-l')(s+l)^{1/2}} \right\} + K' l L^{-1}\left\{ \frac{1}{(s-l')(s+l)^{1/2}} \right\} \right.$$
$$\left. - L^{-1}\left\{ \frac{s^{1/2}}{s-l'} \right\} - l L^{-1}\left\{ \frac{1}{s^{1/2}(s-l')} \right\} \right] \tag{C2}$$

where

$$l' = l/(K'^2 - 1) \tag{C3}$$

Although for the second and fourth terms between the main brackets of eqn. (C2) tabulated inversions are available, we made an alternative derivation in order to avoid complex arguments in the time functions for $K' < 1$.

Starting with the second term on the right-hand side of eqn. (C2), we introduce

$$H(t) = L^{-1}\left\{ \frac{1}{(s-l')(s+l)^{1/2}} \right\} \tag{C4}$$

which can be written as

$$H(t) = L^{-1}\left\{ \frac{1}{(s-l')^{1/2}} \right\} * L^{-1}\left\{ \frac{1}{(s-l')^{1/2}(s+l)^{1/2}} \right\} \tag{C5}$$

where the asterisk denotes the convolution of the two time functions. Using tabulated transforms, $H(t)$ is found to be

$$H(t) = \frac{\exp(l't)}{\pi^{1/2}} \int_0^t \frac{\exp\left[-\tfrac{1}{2}(l+l')u\right]}{(t-u)^{1/2}} I_0\left[\tfrac{1}{2}(l+l')u\right] \, \mathrm{d}u \tag{C6}$$

Expanding I_0 into series according to eqn. (B4) and integrating term-by-term using eqn. (B5) results in

$$H(t) = \exp\left[\tfrac{1}{2}(l'-l)t\right] \sum_{j=0}^{\infty} \frac{(l+l')^{2j}\Gamma(2j+1)t^{2j+1/2}}{4^{2j}\Gamma(2j+3/2)(j!)^2} {}_1F_1\left(\tfrac{1}{2};\, 2j+\tfrac{3}{2};\, \tfrac{1}{2}(l+l')t\right) \tag{C7}$$

Taking into account that $H = 0$ for $t = 0$, we may treat the first term of eqn. (C2) by using

$$L^{-1}\left\{\frac{s}{(s-l')(s+l)^{1/2}}\right\} = \frac{\mathrm{d}H(t)}{\mathrm{d}t} \tag{C8}$$

so that

$$L^{-1}\left\{\frac{s}{(s-l')(s+l)^{1/2}}\right\} = \tfrac{1}{2}(l'-l)H(t) + G(t) \tag{C9}$$

where

$$\begin{aligned} G(t) = \exp\left[\tfrac{1}{2}(l'-l)t\right] \sum_{j=0}^{\infty} \frac{\left[\tfrac{1}{4}(l+l')\right]^{2j}\Gamma(2j+1)t^{2j-1/2}}{\Gamma(2j+\tfrac{1}{2})(j!)^2} \\ \times\Big\{ {}_1F_1(\tfrac{1}{2};\, 2j+3/2;\, \tfrac{1}{2}(l+l')t) \\ + \frac{\tfrac{1}{4}(l+l')t}{(2j+5/2)(2j+3/2)}\, {}_1F_1(3/2;\, 2j+5/2;\, \tfrac{1}{2}(l+l')t)\Big\} \end{aligned} \tag{C10}$$

For treating the two remaining terms on the right-hand side of eqn. (C2), we introduce

$$F(t) = L^{-1}\left\{\frac{1}{s^{1/2}(s-l')}\right\} \tag{C11}$$

The function $F(t)$ can be written as a convolution integral

$$F(t) = \pi^{-1/2}\int_0^t \frac{\exp(l'u)}{(t-u)^{1/2}}\,\mathrm{d}u \tag{C12}$$

which is readily solved using eqn. (B5), yielding

$$F(t) = 2(t/\pi)^{1/2}\, {}_1F_1(1;\, 3/2;\, l't) \tag{C13}$$

Using this result, the inversion of $s^{1/2}/(s-l')$ is easily realized. Because $F(0) = 0$,

$$L^{-1}\left\{\frac{s^{1/2}}{(s-l')}\right\} = F'(t) \tag{C14}$$

so that

$$L^{-1}\left\{\frac{s^{1/2}}{(s-l')}\right\} = \frac{1}{(\pi t)^{1/2}}\, {}_1F_1(1;\, 3/2;\, l't) + \frac{4l'}{3}(t/\pi)^{1/2}\, {}_1F_1(2;\, 5/2;\, l't) \tag{C15}$$

The resulting expression for Φ becomes

$$\Phi(t) = \frac{(\pi t)^{1/2}}{K'^2 - 1}\left[\tfrac{1}{2}K'(l+l')H(t) + K'G(t) - F'(t) - lF(t)\right] \tag{C16}$$

Substitution of the different functions and rearrangement yields eqn. (40).

REFERENCES

1 J. Heyrovský, Polarographie, Springer, Wien, 1941.
2 D.R. Crow, Polarography of Metal Complexes, Academic Press, London, 1969.
3 C.J.M. Kramer and J.C. Duinker (Eds.), Complexation of Trace Metals in Natural Waters, Nijhoff-Junk, The Hague, 1984.
4 J. Koutecký, Collect. Czech. Chem. Commun., 19 (1954) 857.
5 R.R. Dogonadze, Zh. Fiz. Khim., 32 (1958) 2437.
6 M. Lovrić and I. Ružić, J. Electroanal. Chem., 146 (1983) 253.
7 K.S. Crump, J. Ass. Comp. Mach., 23 (1976) 89.
8 IMSL Library, edition 9.2, IMSL, Houston, 1984.
9 H.G. de Jong and H.P. van Leeuwen, J. Electroanal. Chem., 234 (1987) 17.
10 R.F.M.J. Cleven, H.G. de Jong and H.P. van Leeuwen, J. Electroanal. Chem., 202 (1986) 57.
11 S.W. Feldberg in A.J. Bard (Ed.), Electroanalytical Chemistry, Vol. 3, Marcel Dekker, New York, 1969, pp. 199–296.
12 J. Koutecký and R. Brdička, Collect. Czech. Chem. Commun., 12 (1947) 337.
13 M. Abramowitz and I. Stegun, Handbook of Mathematical Functions, Dover, New York, 1965.
14 I.S. Gradshteyn and I.M. Ryzhik, Tables of Series and Integrals, Academic Press, New York, 1981.

J. Electroanal. Chem., 234 (1987) 17–29
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

CHAPTER 3

VOLTAMMETRY OF METAL COMPLEX SYSTEMS WITH DIFFERENT DIFFUSION COEFFICIENTS OF THE SPECIES INVOLVED

PART II. BEHAVIOUR OF THE LIMITING CURRENT AND ITS DEPENDENCE ON ASSOCIATION/DISSOCIATION KINETICS AND LABILITY

HANS G. DE JONG and HERMAN P. VAN LEEUWEN *

Laboratory for Physical and Colloid Chemistry, Wageningen Agricultural University, De Dreijen 6, 6703 BC Wageningen (The Netherlands)

(Received 6th March 1987)

ABSTRACT

The behaviour of the limiting current of a metal complex system for which the diffusion coefficients of the free and complexed metal are different is investigated as a function of the electrolysis time, the association/dissociation rate constants, the stability constant and the diffusion coefficient ratio. For very fast chemical reactions an analytical expression for the limiting current in the time domain is derived. It incorporates the generalized lability condition for a metal complex system. In order to facilitate practical application of the theory developed, Cottrell plots and some working curves are presented as diagnostic tools.

INTRODUCTION

In Part I, a rigorous solution was described for the limiting current of a metal complex system in which the diffusion coefficients of the species involved may be unequal [1]. The solution which is formulated in the Laplace domain is valid for a stationary planar electrode and is restricted to an excess of ligand. It is fully rigorous with respect to the values of the association/dissociation rate constants, thus including any stability constant of the complex.

The aim of the present paper is to elaborate on the new theory and to investigate the behaviour of the limiting current as a function of the electrolysis time (t), the ratio D_{ML}/D_M (ϵ), the stability constant of the complex (K') and the association

---

* To whom correspondence should be addressed.

and dissociation rate constants (k'_a, k_d). The purpose is to gain a thorough understanding of the complications inherent to the chemical kinetics of the complex system and the diffusion coefficients of the species involved. Application of the new insights to practical metal speciation is facilitated by the development of diagnostic tools, such as Cottrell plots and so-called isoflux diagrams. As was found earlier, the condition for lability of metal complexes appears to be of great importance [2] and therefore explicit attention is paid to systems with different lability characteristics.

(I) TIME DEPENDENCE OF THE LIMITING CURRENT

Under the conditions indicated in the Introduction, the expression for the normalized limiting current, Φ, follows from combination of eqns. (19) and (24) of Part I [1]:

$$\Phi(t) = \frac{2(\pi k_d t)^{1/2}}{\epsilon^{1/2}(1+K')} L^{-1}\left\{ \frac{(s+l)^{1/2}(d_- + d_r)(d_+ + d_r)^{1/2} d_r}{s^{1/2}\left[K'\epsilon^{-3/2}s^{1/2}(s+l)^{1/2} + k_d(d_- + d_r)^2(d_+ + d_r)\right]} \right\} \tag{1}$$

with

$$l = k_d(1+K') \tag{2}$$

$$d_\pm = \frac{1}{2}\left[\frac{s}{k_d}(\epsilon^{-1} \pm 1) + \epsilon^{-1} \pm K'\right] \tag{3}$$

$$d_r = \left[d_-^2 + K'\epsilon^{-1}\right]^{1/2} \tag{4}$$

where s is the Laplace variable. Φ represents the limiting current as normalized with respect to the limiting current under the condition that all metal is present as free metal (M).

To investigate the behaviour of $\Phi(t)$ as functions of ϵ, k'_a, k_d and K', eqn. (1) was numerically inverted using a DEC VAX 8600 computer and the FORTRAN subroutine FLINV from the IMSL library [1,3].

(I.1) $\Phi(t)$ as a function of ϵ

In Fig. 1, Φ is plotted vs. t for various values of ϵ. It is clear that the Φ, t relation is strongly governed by association and dissociation kinetics, that is, by the average life times of the complex (ML) and the free metal (M), τ_{ML} ($= k_d^{-1}$) and τ_M ($= k_a'^{-1}$) respectively. According to the magnitudes of τ_{ML} and τ_M relative to t, three characteristic regimes can be distinguished and these are discussed in the following.

(I.1.1) The static regime (τ_M, $\tau_{ML} \gg t$)

The first regime is the static or non-dynamic regime, which is encountered if τ_{ML}

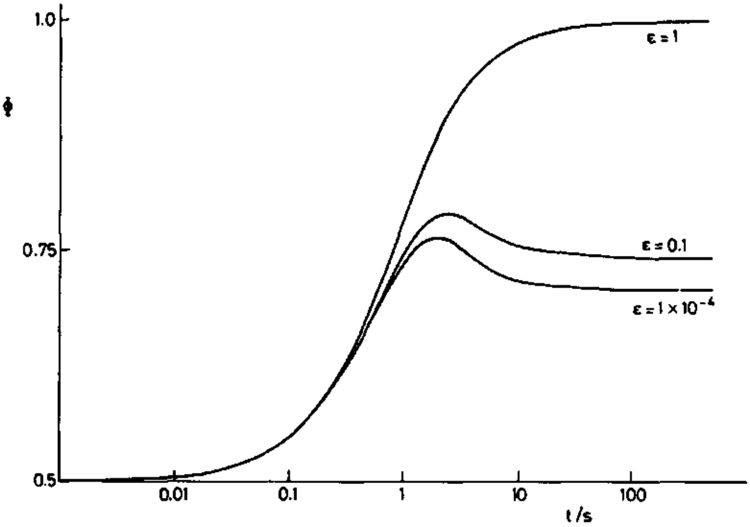

Fig. 1. Normalized limiting current (Φ) as a function of the electrolysis time (t) for various values of D_{ML}/D_M (ϵ). $K'=1$ and $k_d = 1$ s^{-1}.

and τ_M are much larger than t. Here, the short time limit of eqn. (1) applies and this reads simply [1]:

$$\Phi(t) = (1 + K')^{-1} \tag{5}$$

The result $(1 + K')^{-1}$ represents the equilibrium fraction of M, indicating that in the static region only the diffusion of M is measured. We note that expression (5) for Φ corresponds to a limiting current proportional to $D_M^{1/2} c_M^* / t^{1/2}$, where c_M^* is the equilibrium concentration of M. The chemical equilibrium is frozen so that during the experiment, disequilibration in the vicinity of the electrode does not lead to any significant formation of M. This static behaviour may be understood in terms of the average life times of M and ML. Since $\tau_{ML} \gg t$, the electroinactive ML does not dissociate to any significant extent during the actual electrolysis process so that there is no contribution of ML to the limiting current. On the other hand, since $\tau_M \gg t$, M can be reduced at the electrode before it associates with L so that we obtain the result of a diffusion-limited current proportional to c_M^*.

(I.1.2) The semi-dynamic regime (τ_M, $\tau_{ML} \approx t$)

The intermediate regime is the situation in which τ_{ML} and τ_M have an order of magnitude comparable to that of t. It is denoted here as the semi-dynamic regime and it shows the most involved Φ, t relation. On the time-scale of the experiment, some of the complex species dissociate and some of the M produced will be reduced at the electrode. Close to the electrode, c_{ML} exceeds the value prescribed by the chemical equilibrium (Figs. 2A1 and 2B1) which means that the dissociation rate

$k_d c_{ML}$ exceeds the association rate $k_a' c_M$. Consequently, the limiting current is higher than that in the static case. As t is increased, more complex is allowed to dissociate and therefore Φ grows with time at the onset of the semi-dynamic regime. It is also evident from Fig. 1 that the initial increase of Φ is independent of ϵ. In this situation the diffusion of the free metal is much faster than its generation by dissociation of ML. Close to the electrode, the net concentration of M is therefore kinetically limited. The complex is electroinactive and thus the net ML concentration is kinetically limited, too. At the onset of the semi-dynamic regime, only a relatively small concentration gradient for ML is developed (Figs. 2A1 and 2B1). In this situation, D_{ML} is irrelevant and the limiting current density i is still proportional to $D_M^{1/2}$ but no longer to c_M^* and $t^{-1/2}$. When t is increased further, the concentration gradient of ML is much more pronounced (Figs. 2A2 and 2B2), due to significant depletion of ML close to the electrode. The rate of diffusional transport of ML becomes significant compared to the depletion rate, and in Fig. 1 the curves for different ϵ no longer coincide. Φ increases with increasing ϵ because

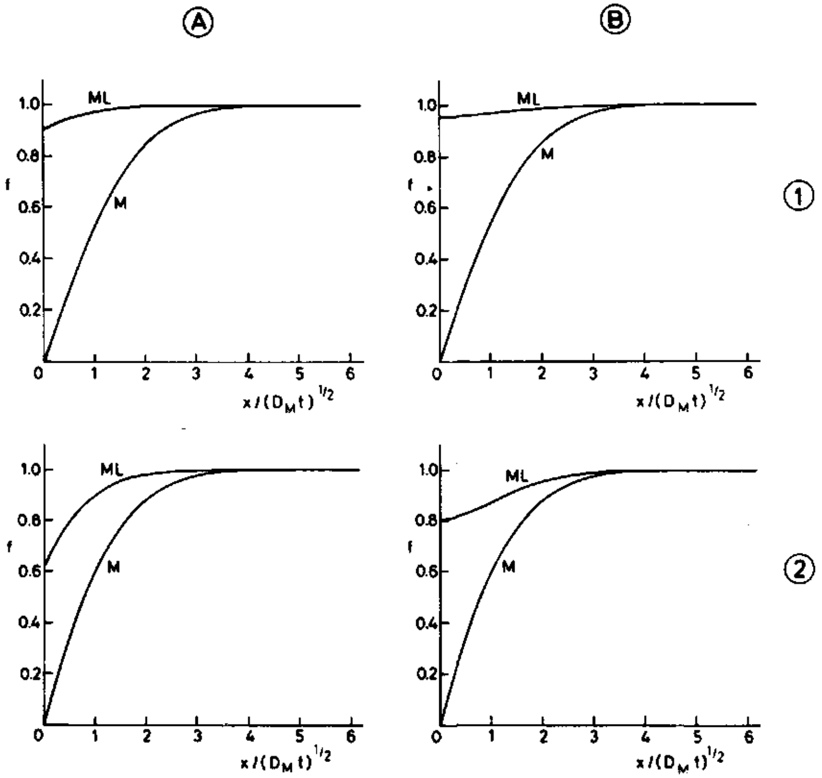

Fig. 2. Concentration profiles for the free metal (M) and complex (ML) as a function of the time. $K' = 1$, $k_d = 1\ s^{-1}$ for each figure. Series A for $\epsilon = 0$; series B for $\epsilon = 1$. Both series: $t = 0.1$ s (1); 0.5 s (2); 2 s (3); 100 s (4).

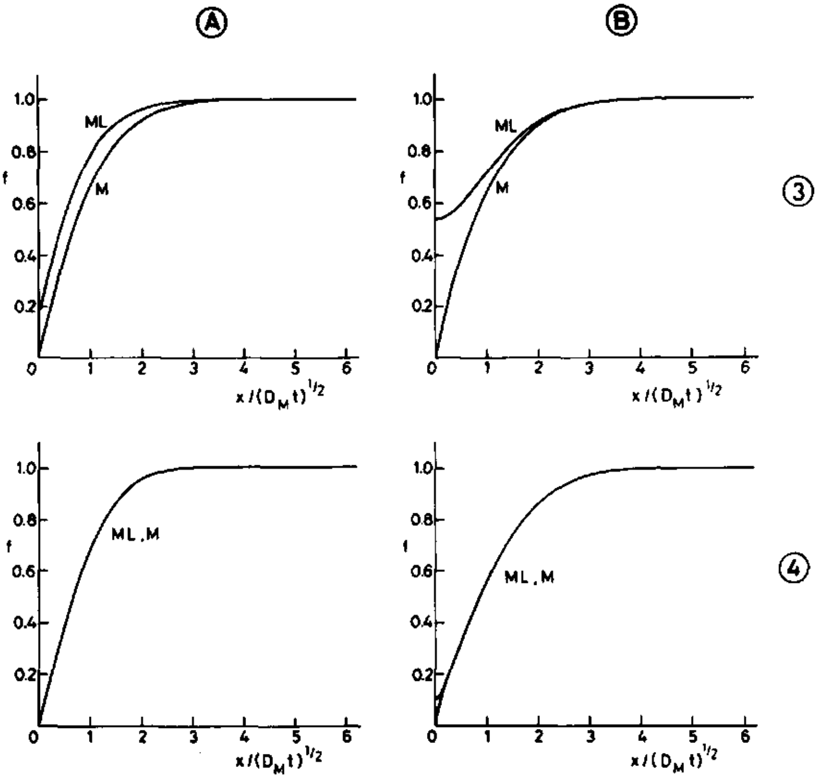

Fig. 2 (continued).

the higher the value of ϵ, the more complex is transported towards the electrode where it can dissociate to yield more electroactive M.

On increasing t further, a maximum in Φ is reached. This maximum is most pronounced for the smaller ϵ values. With ϵ approaching 1, the maximum vanishes. The occurrence of the maximum may be explained as follows. Consider some electrolysis time which is smaller than the time of the maximum. Then c_{ML} exceeds the local equilibrium value $K'c_M$ (Figs. 2A2 and 2B2). Therefore, the gradient of M in the vicinity of the electrode is determined mainly by dissociation of ML and diffusion of M, the association reaction and diffusion of ML still being relatively unimportant. If t is increased to values beyond the maximum, the excess of ML as compared to the local equilibrium concentration disappears (Fig. 2A3). Compared to the former situtION, the association of M with L has become much more important. In this case, the gradient of M is determined not only by diffusion of M and dissociation of ML but also by association of M. The net result is that the gradient of M, and consequently Φ, increases less with t or even decreases in the case of the smaller ϵ values. If ϵ approaches 1, the "excess" of ML in the vicinity of the electrode persists at higher t values because the rate of diffusion of ML is higher (compare Figs. 2A3 and 2B3) and the depletion of ML proceeds more gradually than at low values of ϵ. Typically for $\epsilon < 1$, there is a discrepancy between the depletion layers for ML and M in the sense that the former lags behind (compare Figs. 2A2 and 2A3 with 2A4). The consequence is that, before reaching the final situation of a joint mean diffusion layer, the strongly growing influence from ML results in an "overshoot" in the flux of ML and M. This phenomenon, which is a typical transient effect, is clearly illustrated by the profile of ML in Fig. 2A3.

(I.1.3) The dynamic regime (τ_M, $\tau_{ML} \ll t$)

In the long time limit, t largely exceeds the average life times of M and ML. Here, the chemical state of the metal changes many times during the experiment. The dynamic behaviour of the metal complexation equilibrium is typical for this regime and therefore it is denoted as the "dynamic" regime. Under the present conditions, i.e. with $\tau_{\mathrm{M}} \ll t$ and $\tau_{\mathrm{ML}} \ll t$, eqn. (1) can be simplified by combining eqns. (24) and (45) of ref. 1:

$$\Phi(t) = \frac{(\pi k_{\mathrm{d}} t)^{1/2} (\epsilon^{-1} + K')^{3/2} l^{1/2}}{(1 + K')} L^{-1} \left\{ \frac{1}{\left[K' l^{1/2} s^{1/2} + k_{\mathrm{d}} \epsilon^{-1/2} (\epsilon^{-1} + K') \right] s^{1/2}} \right\} \tag{6}$$

which can be transformed into

$$\Phi(t) = \frac{(\pi k_{\mathrm{d}} t)^{1/2} (\epsilon^{-1} + K')^{3/2}}{K'(1 + K')} \exp(\Lambda^2 t) \operatorname{erfc}(\Lambda t^{1/2}) \tag{7}$$

where

$$\Lambda = \frac{k_{\mathrm{d}}^{1/2} \epsilon^{-1/2} (\epsilon^{-1} + K')}{K'(1 + K')^{1/2}} \tag{8}$$

An expression similar to eqn. (7) was tentatively formulated by Tamamushi and Sato [4]. For $\epsilon = 1$, i.e. $D_{\mathrm{M}} = D_{\mathrm{ML}}$, eqn. (7) yields the same flux as that obtained by Koutecký and Brdička [5]. From eqn. (7), two interesting limiting cases arise, i.e. $\Lambda t^{1/2} \gg 1$ and $\Lambda t^{1/2} \ll 1$, which are discussed below.

(I.1.3.a) The case $\Lambda t^{1/2} \ll 1$ (the non-labile system). The experfc function in eqn. (7) can be expanded in a series:

$$\exp(\Lambda^2 t) \operatorname{erfc}(\Lambda t^{1/2}) = 1 - \frac{2 \Lambda t^{1/2}}{\pi^{1/2}} + \Lambda^2 t + \ldots \tag{9}$$

Under the condition that

$$\Lambda t^{1/2} \ll 1 \tag{10}$$

eqn. (7) reduces to

$$\Phi(t) = \frac{(\pi k_{\mathrm{d}} t)^{1/2} (\epsilon^{-1} + K')^{3/2}}{K'(1 + K')} \tag{11}$$

and a purely kinetic current is obtained. For very large K', eqn. (11) can be reduced to

$$\Phi(t) = (\pi k_d t/K')^{1/2} \tag{12}$$

which can be rearranged to

$$\frac{i(t)}{nF} = \frac{D_M^{1/2} c_T^* \Phi(t)}{(\pi t)^{1/2}} = k_d c_{ML}^* \left(\frac{D_M}{k_a'}\right)^{1/2} \tag{13}$$

where i is the current density, $c_T^* = c_M^* + c_{ML}^*$ and n and F have their usual meanings. This result is identical to the expression derived using the reaction layer concept, valid for a system which is both dynamic and non-labile.

(I.1.3.b) The case $\Lambda t^{1/2} \gg 1$ (the labile system). For large arguments the experfc function in eqn. (7) can be approximated by [6]:

$$\exp(\Lambda^2 t)\ \mathrm{erfc}(\Lambda t^{1/2}) \sim \frac{1}{\Lambda(\pi t)^{1/2}}\left[1 - \frac{1}{2\Lambda^2 t} + \frac{3}{4\Lambda^4 t^2} - \ldots\right] \tag{14}$$

If $\Lambda t^{1/2}$ is so large that

$$\Lambda^2 t \gg 1 \tag{15}$$

then

$$\Phi(t) = \frac{(1+\epsilon K')^{1/2}}{(1+K')^{1/2}} \tag{16}$$

which is easily rearranged to

$$\frac{i(t)}{nF} = \frac{\bar{D}^{1/2} c_T^*}{(\pi t)^{1/2}} \tag{17}$$

where $\bar{D}$ is the mean diffusion coefficient of the complex system, so that a purely diffusion-controlled current is obtained.

Inequality (15) may be identified as a lability criterion for the metal complex system as a whole, i.e. ML plus M. It compares the situation where the limiting current is governed by association/dissociation kinetics (eqn. 11) with the situation where the limiting current is purely controlled by diffusion (eqn. 16). A labile system obeys condition (15) and its association/dissociation kinetics are so fast that the levels of c_M and c_{ML} are mass transport controlled. An analogous expression for the lability criterion was derived in the Laplace domain [1].

In earlier studies [7,8] the condition for electrochemical lability of a complex species was derived as

$$\frac{k_d t^{1/2}}{k_a'^{1/2}} \gg 1 \tag{18}$$

For a complex system with $D_M \neq D_{ML}$, the lability criterion was tentatively extended to [2]

$$\frac{k_d \epsilon^{-1/2} t^{1/2}}{k_a'^{1/2}} \gg 1 \tag{19}$$

It should be stressed that condition (19) is formulated for a situation in which $K' \gg 1$ and therefore it is concerned with the properties of the complex only, i.e. it determines whether or not the species ML is labile. The rigorous condition (15) is a lability criterion for the complex system as a whole, i.e. it incorporates any distribution over the species M and ML. The relationship between the different conditions is clarified further by noting that condition (19) is in fact a special limit of condition (15). For $K' \to \infty$, i.e. for systems with ML only, condition (15) reduces to

$$\frac{k_d t}{\epsilon K'} \gg 1 \tag{20}$$

which is similar to condition (19). Thus the new lability criterion (15) may be considered as a generalized criterion for the complex system.

The lability condition is met by the system presented in Fig. 1 for large t values and consequently the curves are horizontal, with Φ corresponding to the value predicted by eqn. (16). Further examples of lability and non-lability will be discussed below.

(I.1.4) Cottrell plots

In pulse voltammetry, Cottrell plots are useful for investigating some of the characteristics of the electrochemical process [9]. In Fig. 3, some typical Cottrell plots are presented for a static system (i), a semi-dynamic system (ii) and a labile system (iii). The two straight lines represent the two limiting cases: (i) and (iii), their slopes corresponding to $(1 + K')^{-1}$ (eqn. 5) and $[(1 + \epsilon K')/(1 + K')]^{1/2}$ (eqn. 16), respectively. At very short times, the curve for the semi-dynamic system approaches the static limit (i), and for large t it reaches the labile limit (iii). In the intermediate region, the semi-dynamic curve is characteristic. In the time domain of the typical maximum in the Φ vs. t plots, the semi-dynamic curve exceeds the labile limit. From Fig. 3 it is obvious that for both the static and the labile case, the straight lines can be extrapolated to the origin. This criterion is useful for tracing the dynamic behaviour of a particular system. If the experimental data seem to yield a straight line with a significant intercept, either positive or negative, then the system could fall in some kinetic category, e.g. semi-dynamic or dynamic but not labile. For discrimination between static and labile behaviour, it is necessary to compare the half-wave potential for the complex system with that for M. A comprehensive discussion of the behaviour of the potential characteristics for all the cases considered here will be presented in a forthcoming paper [10].

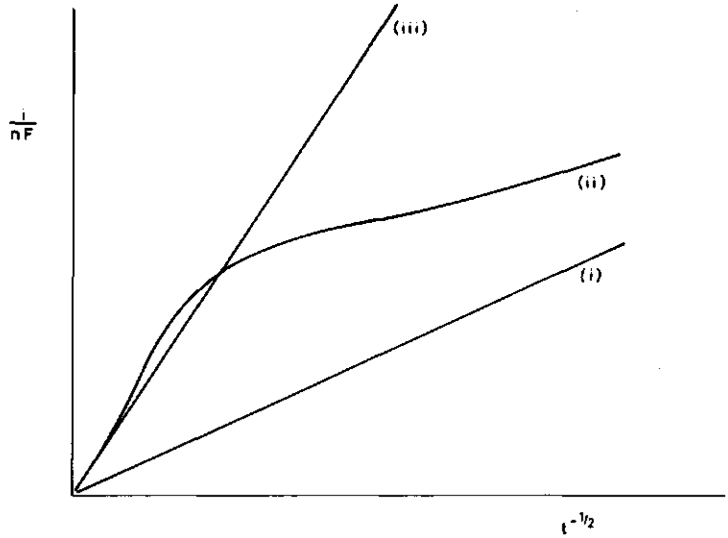

Fig. 3. Cottrell plots for a static system (i), a semi-dynamic system (ii) and a labile system (iii).

(I.2) $\Phi(t)$ as a function of k_d

The discussion so far has been concerned with the time dependence of the limiting current at fixed values of k_d and K'. In Fig. 4, Φ vs. t is plotted for various values of k_d. Completely to the left, the static limit is found again. The three

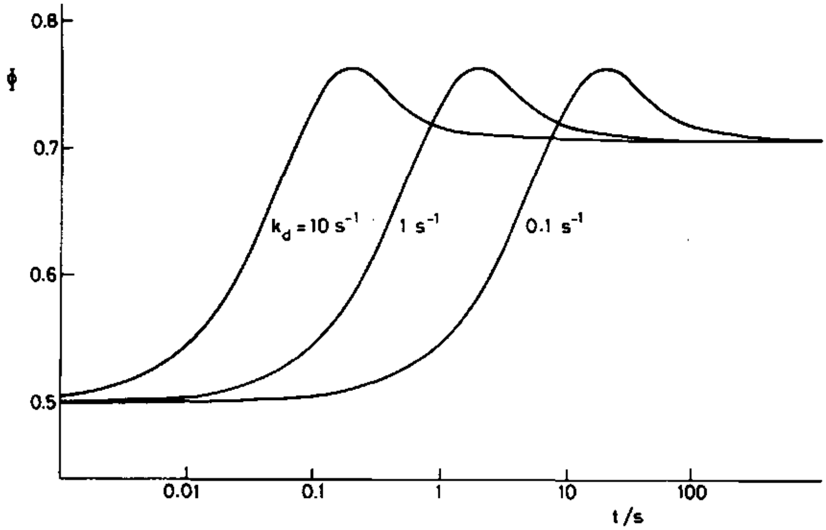

Fig. 4. Φ, t plots for various values of k_d. $K' = 1$ and $\epsilon = 10^{-4}$.

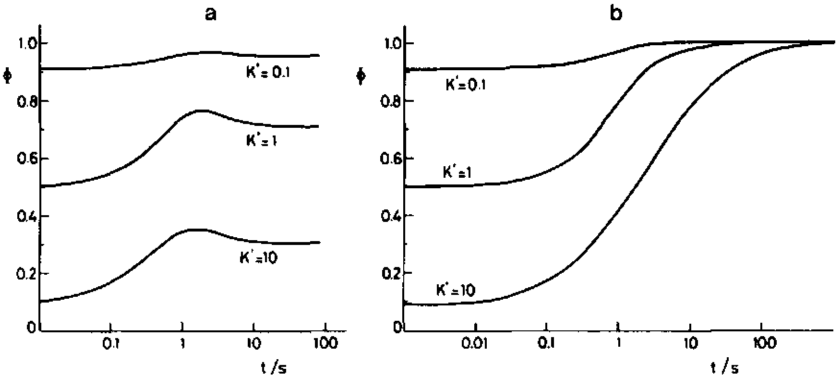

Fig. 5. Φ, t plots for various values of K' and ϵ. $k_d = 1\ s^{-1}$, $\epsilon = 10^{-4}$ (a); $\epsilon = 1$ (b).

curves are constructed for the same K', consequently the equilibrium concentration of M is the same in all three cases and therefore the curves coincide in the short time limit. At very large times, the labile limit is found. The different curves in Fig. 4 hold for the same K' and ϵ and therefore $\overline{D}$ is the same, so that the curves coincide in the long time limit. With decreasing k_d values, the Φ vs. t curve shifts to the right, i.e. to higher values of the actual electrolysis time. Simultaneously, τ_{ML} increases and consequently the formation of M by dissociation of ML decreases. This results in a shift of the Φ, t curve towards higher t values. The similarity of the shapes of the curves is related to the fact that K' is kept constant, which means that k_d and k_a' change by the same factor. Plotting Φ vs. t for different k_d and constant k_a' yields different pictures which are less transparent. The maxima in the ϕ, t curves are found at values close to $2k_d^{-1}$ (see also Fig. 5). This implies that the effects of depletion of the excess ML relative to equilibrium conditions are highest when t reaches values of the order of τ_{ML}.

(I.3) $\Phi(t)$ as a function of K'

In Fig. 5, Φ is plotted vs. t for various values of K' and ϵ. It is seen that in the short time limit, Φ is independent of ϵ because only c_M^* is relevant. Since c_M^* decreases with increasing K', we observe a strong dependence of Φ on K' in this region. In the labile limit, differences between the curves in Figs. 5a and 5b are observed. In Fig. 5b the labile limit of Φ is the same for different values of K'. Here, the mean diffusion coefficient is equal to D_M because $\epsilon = 1$. If $\epsilon < 1$, $\overline{D}$ decreases with increasing K', approaching the minimum value D_{ML} for extremely large K'. For $\epsilon = 1$, the Φ, t curves show no maximum, as pointed out earlier. With K' values approaching zero, the maximum vanishes because most of the metal is present as M so that the interconversion between ML and M loses its relevance. It should be noted that the position of the maximum does not depend on the value of

K' as long as k_d is kept constant. This shows that τ_{ML} ($= 1/k_d$) rather than τ_M ($= 1/k'_a$) is the leading parameter in this respect.

(II) ILLUSTRATION OF LABILITY CONDITIONS

For a metal complex system to behave in a labile manner, it must satisfy condition (15). This requirement implies dynamic behaviour, i.e. only dynamic systems can be classified as labile or non-labile. If we allow an error of 1% in the approximation of Φ by eqn. (16), condition (15) becomes $\Lambda^2 t \geqslant 50$. The significance of this condition is illustrated by plotting Φ vs. ϵ for systems with different values of $k_d t$ (Fig. 6). Curve a is constructed for a labile system. Both $k'_a t$ and $k_d t$ are large compared to one (10^5 and 10^4, respectively) and $\Lambda^2 t = 10^3$ for $\epsilon = 1$, which fulfils the lability condition in the entire ϵ domain. Curve b is constructed for a dynamic system since both $k'_a t$ and $k_d t$ are large, i.e. 10^3 and 10^2, respectively. Contrary to the former case, $\Lambda^2 t \approx 10$ for $\epsilon = 1$ and the lability criterion is not fulfilled. Only for $\epsilon < 0.3$ is the lability criterion fulfilled, and we observe that indeed curves a and b almost coincide below this value. Curves a and b clearly demonstrate that a dynamic system does not necessarily behave in a labile manner.

Curve c is typical for the semi-dynamic situation: $k'_a t = 50$ and $k_d t = 5$. The typical phenomenon of exceeding the Φ value for the labile limit (corresponding to the maximum in the Φ, t characteristic) shows up for the lower values of ϵ. Ranging to higher values of ϵ, Φ increases less than in the dynamic case because c_M is governed more strongly by the association/dissociation kinetics. Therefore the

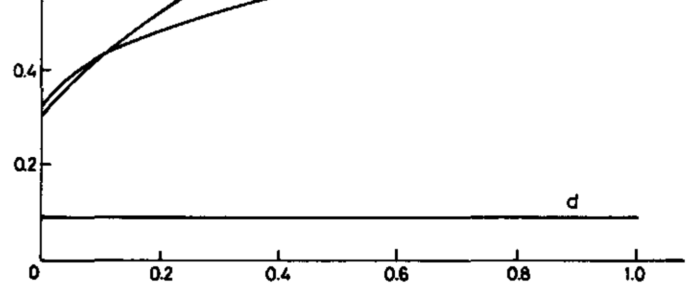

Fig. 6. Φ, ϵ plots for $K' = 10$. $k_d t = 10^4$ (a), 10^2 (b), 5 (c) and 10^{-4} (d).

increase in the diffusional transport of ML inherent to an increase in ϵ exhibits a smaller effect on c_M in the vicinity of the electrode (cf. Fig. 2).

Curve d represents the static case, where $k'_a t$ and $k_d t$ are small, i.e. 10^{-3} and 10^{-4}, respectively. Here, Φ is equal to the limit $(1 + K')^{-1}$ so that ϵ is irrelevant.

(III) WORKING CURVES FOR SPECIATION PRACTICE

A convenient way to report results of (semi-)numerical analyses is via the so-called working curves [9]. In this section, some working curves are presented as examples for use in speciation practice. It should be emphasized that the curves depend strongly on the kinetic nature of the system. Only in the static and the labile limits is it practical to make use of working curves. In the kinetic case, curves would be necessary for every discrete set of k'_a, k_d and t values.

One way to construct working curves is to plot Φ vs. pK'. This is shown in Fig. 7 for a static and a labile system. As discussed earlier, Φ is proportional to $D_M^{1/2} c_M^*$ for a static system, and consequently Φ. vs. K' yields a curve independent of ϵ. In the case of large pK', virtually all of the metal is present in the uncomplexed form and therefore Φ is close to unity. In Fig. 7b, Φ is plotted vs. pK' for a labile system. The differences with Fig. 7a are striking. There exists a clear dependence of Φ on ϵ because $\overline{D}$ is operative. The differences between the various curves in Fig. 7b increase with increasing K'. For large K' and $\epsilon < 1$, $\overline{D}$ approaches the limiting value D_{ML} and the current is then proportional to $D_{ML}^{1/2} c_{ML}^* / t^{1/2}$. For low K', virtually no ML is present in the solution, so that the ϵ dependence disappears and the curves in Fig. 7b coincide.

In metal speciation practice, one often has some crude idea about the order of magnitude of K' and/or ϵ. In such a case, isoflux diagrams may be helpful in determining K' and ϵ more accurately. Φ is obtained experimentally as the ratio between the current for the complex system and the current obtained under

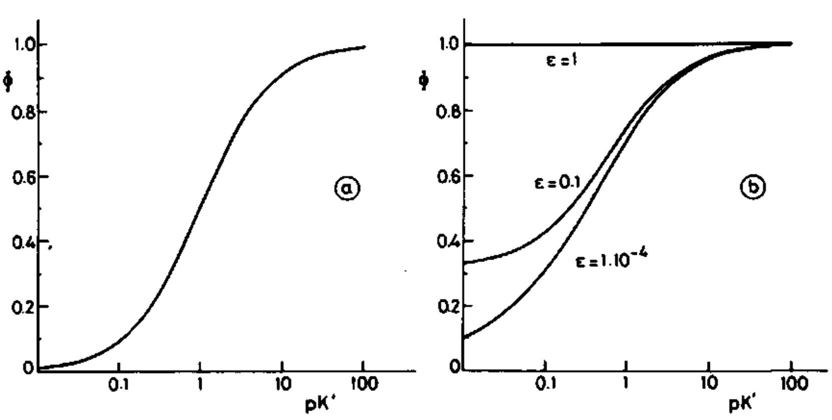

Fig. 7. Φ, pK' plots for a static system (a) and a labile system (b).

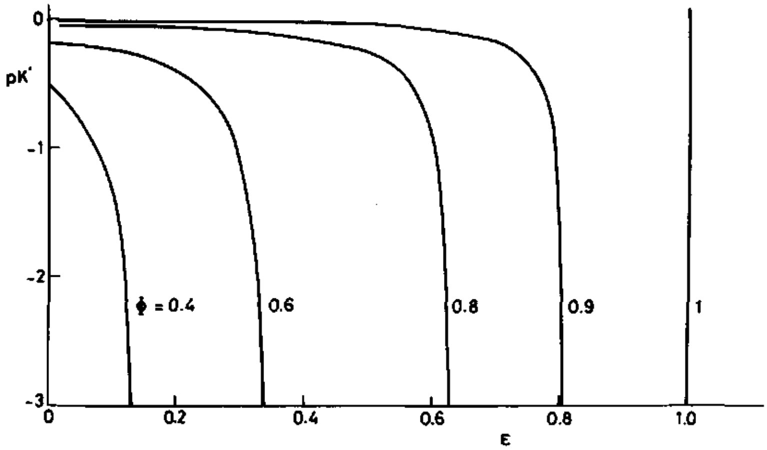

Fig. 8. Isoflux diagrams for a labile system, showing pK' as a function of ϵ at given values of Φ.

conditions where all of the metal is in the uncomplexed form (often realized by remeasuring at very low pH). In Fig. 8, isoflux diagrams are presented for a labile system. These diagrams are suitable for not too extreme values of K'. For a given ϵ, one can read the stability constant of the complex from the diagram using the measured value of Φ. In cases of kinetic behaviour, one may solve the speciation problem by fitting the theoretical equation for Φ to the experimental data.

REFERENCES

1 H.G. de Jong, H.P. van Leeuwen and K. Holub, J. Electroanal. Chem., 234 (1987) 1.
2 R.F.M.J. Cleven, H.G. de Jong and H.P. van Leeuwen, J. Electronanal. Chem., 202 (1986) 57.
3 IMSL Library, edition 9.2, IMSL, Houston, 1984.
4 R. Tamamushi and G.P. Sato in P. Zuman (Ed.), Progress in Polarography, Vol. 3, Interscience, New York, 1972, p. 1.
5 J. Koutecký and R. Brdička, Collect. Czech. Chem. Commun., 12 (1947) 337.
6 M. Abramowitz and I. Stegun, Handbook of Mathematical Functions, Dover, New York, 1965.
7 W. Davison, J. Electroanal. Chem., 87 (1978) 395.
8 H.P. van Leeuwen, J. Electroanal. Chem., 99 (1979) 93.
9 A.J. Bard and L.R. Faulkner, Electrochemical Methods, Wiley, New York, 1980.
10 H.G. de Jong and H.P. van Leeuwen, J. Electroanal. Chem., 235 (1987) 1.

J. Electroanal. Chem., 235 (1987) 1–10
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

CHAPTER 4

VOLTAMMETRY OF METAL COMPLEX SYSTEMS WITH DIFFERENT DIFFUSION COEFFICIENTS OF THE SPECIES INVOLVED

PART III. THE CURRENT–POTENTIAL RELATION FOR THE GENERAL CASE INCLUDING ASSOCIATION / DISSOCIATION KINETICS

HANS G. DE JONG and HERMAN P. VAN LEEUWEN *

*Laboratory for Physical and Colloid Chemistry, Agricultural University, De Dreijen 6,
6703 BC Wageningen (The Netherlands)*

(Received 30th April 1987)

ABSTRACT

An exact equation is derived for the current–potential relation of a metal complex system in which the diffusion coefficients of the different species are unequal. The equation is formulated in the Laplace domain and is valid in the case of excess ligand and reversible reduction at a stationary planar electrode. It is rigorous with respect to the values of the association and dissociation rate constants and the diffusion coefficients of the species. In some limiting cases, analytical expressions in the time domain were obtained. In cases where derivation of analytical time functions was impossible, half-wave potentials were calculated after numerical inversion of the complete current–potential relation.

INTRODUCTION

In the previous papers of this series, we presented a rigorous treatment of the limiting current of a metal complex system and its application to metal speciation [1,2]. As a further step, we want to extend the theory to the complete polarographic wave, which will enable us to employ both the current and the potential characteristics. The importance of this was indicated many years ago by Heyrovský and Ilkovič [3].

In 1951, DeFord and Hume presented their classical paper on the analysis of the half-wave potential shift in terms of the stability constants of the complex ions involved [4]. This treatment is limited to complexes which are in equilibrium with their components at any distance from the electrode surface, viz. to labile com-

---

* To whom correspondence should be addressed.

plexes. Current–potential relations for the limiting case with equal diffusion coefficients of the species involved have been derived for expanding planar or spherical electrodes [5–9]. The result is given as an approximate analytical expression with relatively simple functions [5–7] or in terms of an involved series expansion [8,9]. For semi-infinite diffusion towards a planar electrode, Lovrić and Ružić [10] derived a relation which is restricted to large stability constants and not too different values of the diffusion coefficients of the species.

In this paper, we derive an equation for the current–potential relation in the case of semi-infinite diffusion to a planar electrode which is valid for any set of values of the association and dissociation rate constants and diffusion coefficients of the species. The equation is formulated in the Laplace domain, and for some limiting cases, analytical inversion to the time domain will be attempted so that explicit operational equations for the half-wave potential can be given. Where analytical inversion failed, the half-wave potential was obtained from the general current–potential relation by a numerical procedure.

FORMULATION OF THE PROBLEM

Consider a system with an electroactive metal ion M and a ligand L which may form an electroinactive complex ML:

$$\mathrm{M} + \mathrm{L} \underset{k_\mathrm{d}}{\overset{k_\mathrm{a}}{\rightleftarrows}} \mathrm{ML} \tag{1}$$

$$\mathrm{M} + n\,e^- \rightleftarrows \mathrm{M}^\circ \tag{2}$$

The charges of the ionic species are omitted for clarity. M° denotes the reduced metal. Assume that the preceding complexation reaction is pseudo-first order (excess of ligand) with the equilibrium constant:

$$K' = c^*_\mathrm{ML}/c^*_\mathrm{M} = k'_\mathrm{a}/k_\mathrm{d} = k_\mathrm{a}c^*_\mathrm{L}/k_\mathrm{d} \tag{3}$$

where c^* denotes the bulk concentration and k'_a and k_d denote the rate constants for association and dissociation, respectively.

For semi-infinite diffusion of the species to/from a stationary planar electrode, the transport equations read:

$$\partial c_\mathrm{M}/\partial t = D_\mathrm{M}\, \partial^2 c_\mathrm{M}/\partial x^2 - k'_\mathrm{a}c_\mathrm{M} + k_\mathrm{d}c_\mathrm{ML} \tag{4}$$

$$\partial c_\mathrm{ML}/\partial t = D_\mathrm{ML}\, \partial^2 c_\mathrm{ML}/\partial x^2 + k'_\mathrm{a}c_\mathrm{M} - k_\mathrm{d}c_\mathrm{ML} \tag{5}$$

$$\partial c_{\mathrm{M}^\circ}/\partial t = D_{\mathrm{M}^\circ}\, \partial^2 c_{\mathrm{M}^\circ}/\partial x^2 \tag{6}$$

with boundary conditions:

$$t = 0 \quad x \geqslant 0 \qquad \begin{cases} c_\mathrm{ML}/c_\mathrm{M} = K' & \text{(7a)} \\ c_{\mathrm{M}^\circ} = 0 & \text{(7b)} \end{cases}$$

$$t > 0 \quad x \to \infty \qquad c_\mathrm{M} = c^*_\mathrm{M}, \quad c_\mathrm{ML} = c^*_\mathrm{ML}, \quad c_{\mathrm{M}^\circ} = 0 \tag{8}$$

At $t = 0$, the potential E is changed instantaneously to a value somewhere in the reduction wave. If it is assumed that the system is electrochemically reversible, so that c_{M° and c_{M} at the electrode surface are related by Nernst's law, then the boundary conditions at the electrode surface are:

$$t > 0, \quad x = 0 \quad \begin{cases} c_{\mathrm{M}}/c_{\mathrm{M}^\circ} = \theta = \exp\left[(nF/RT)(E - E^\circ)\right] & \text{(9a)} \\ D_{\mathrm{M}}\, \partial c_{\mathrm{M}}/\partial x + D_{\mathrm{M}^\circ}\, \partial c_{\mathrm{M}^\circ}/\partial x = 0 & \text{(9b)} \\ \partial c_{\mathrm{ML}}/\partial x = 0 & \text{(9c)} \end{cases}$$

This formulation of boundary conditions (8) and (9b) implies that the diffusion of M° is directed into the solution. In the case of amalgam formation, M° diffuses in the same direction as M, but the expressions are, of course, essentially the same.

After transformation into the Laplace domain, the transport eqns. (4)–(6) read:

$$\frac{\mathrm{d}^2\bar{c}_{\mathrm{M}}}{\mathrm{d}x^2} = \frac{s + k'_{\mathrm{a}}}{D_{\mathrm{M}}}\bar{c}_{\mathrm{M}} - \frac{k_{\mathrm{d}}}{D_{\mathrm{M}}}\bar{c}_{\mathrm{ML}} - \frac{c^*_{\mathrm{M}}}{D_{\mathrm{M}}} \tag{10}$$

$$\frac{\mathrm{d}^2\bar{c}_{\mathrm{ML}}}{\mathrm{d}x^2} = -\frac{k'_{\mathrm{a}}}{D_{\mathrm{ML}}}\bar{c}_{\mathrm{M}} + \frac{s + k_{\mathrm{d}}}{D_{\mathrm{ML}}} - \frac{c^*_{\mathrm{ML}}}{D_{\mathrm{ML}}} \tag{11}$$

$$\frac{\mathrm{d}^2\bar{c}_{\mathrm{M}^\circ}}{\mathrm{d}x^2} = \frac{s}{D_{\mathrm{M}^\circ}}\bar{c}_{\mathrm{M}^\circ} \tag{12}$$

where s is the Laplace transform parameter and the overbar denotes a transformed variable. Using a linear combination of $\bar{c}_{\mathrm{M}}$ and $\bar{c}_{\mathrm{ML}}$ according to d'Alembert's method, the simultaneous differential eqns. (10) and (11) can be solved [1].

We define

$$\Psi_\pm = \bar{c}_{\mathrm{ML}} \pm k_\pm \bar{c}_{\mathrm{M}} \tag{13}$$

with

$$k_\pm = d_- \pm d_{\mathrm{r}} \tag{14}$$

$$d_\pm = \tfrac{1}{2}\left[(s/k_{\mathrm{d}})(\epsilon^{-1} \pm 1) + \epsilon^{-1} \pm K'\right] \tag{15}$$

$$d_{\mathrm{r}} = \left(d_-^2 + K'\epsilon^{-1}\right)^{1/2} \tag{16}$$

where

$$\epsilon = D_{\mathrm{ML}}/D_{\mathrm{M}} \tag{17}$$

Then the solution to eqns. (10) and (11) reads:

$$\Psi_\pm = \frac{c^*_{\mathrm{ML}} + k_\pm \epsilon c^*_{\mathrm{M}}}{s + k_{\mathrm{d}} - k_\pm k'_{\mathrm{d}}\epsilon} + A_\pm(s)\exp\left[-\left(\frac{s + k_{\mathrm{d}}}{D_{\mathrm{ML}}} - \frac{k_\pm k_{\mathrm{d}}}{D_{\mathrm{M}}}\right)x\right] \tag{18}$$

Equation (12) is solved straightforwardly to give

$$\bar{c}_{\mathrm{M}^\circ} = B(s)\exp\left[-(s/D_{\mathrm{M}^\circ})^{1/2}x\right] \tag{19}$$

The unknowns $A_+(s)$, $A_-(s)$ and $B(s)$ may be found by applying boundary conditions (9a)–(9c), e.g. in the form

$$\frac{\Psi_+(0)-\Psi_-(0)}{k_+-k_-}=\theta B(s) \tag{20a}$$

$$\frac{D_\mathrm{M}}{k_-}\left(\frac{\mathrm{d}\Psi_-}{\mathrm{d}x}\right)_{x=0}-D_{\mathrm{M}^\circ}^{1/2}s^{1/2}B(s)=0 \tag{20b}$$

$$k_+\left(\frac{\mathrm{d}\Psi_-}{\mathrm{d}x}\right)_{x=0}-k_-\left(\frac{\mathrm{d}\Psi_+}{\mathrm{d}x}\right)_{x=0}=0 \tag{20c}$$

For calculation of the gradient $(\mathrm{d}\bar{c}_\mathrm{M}/\mathrm{d}x)_{x=0}$ it is sufficient to solve $A_-(s)$. The result is conveniently expressed as

$$A_-(s)=[A_-(s)]_\mathrm{l}/\chi(s) \tag{21}$$

where

$$[A_-(s)]_\mathrm{l}=\frac{c_\mathrm{M}^*}{k_\mathrm{d}}\frac{\left(d_-+d_\mathrm{r}+K'\epsilon^{-1}\right)-\left(d_--d_\mathrm{r}+K'\epsilon^{-1}\right)(d_+-d_\mathrm{r})(d_++d_\mathrm{r})^{-1}}{(d_+-d_\mathrm{r})-(d_-+d_\mathrm{r})\left(d_+^2-d_\mathrm{r}^2\right)^{1/2}(d_--d_\mathrm{r})^{-1}} \tag{22}$$

which is the $A_-(s)$ value found for limiting current conditions, as was extensively discussed before [1], and

$$\chi(s)=1+\frac{2\theta\xi k_\mathrm{d}^{1/2}\left(d_+^2-d_\mathrm{r}^2\right)^{1/2}d_\mathrm{r}}{s^{1/2}\left[(d_-+d_\mathrm{r})(d_++d_\mathrm{r})^{1/2}-(d_--d_\mathrm{r})(d_+-d_\mathrm{r})^{1/2}\right]} \tag{23}$$

with

$$\xi=(D_\mathrm{M}/D_{\mathrm{M}^\circ})^{1/2}$$

Now using the direct relation between $(\mathrm{d}\bar{c}_\mathrm{M}/\mathrm{d}x)_{x=0}$ and $(\mathrm{d}\Psi_-/\mathrm{d}x)_{x=0}$, finally we obtain for the gradient

$$\begin{aligned}\left(\frac{\mathrm{d}\bar{c}_\mathrm{M}}{\mathrm{d}x}\right)_{x=0}=\frac{2c_\mathrm{M}^*}{D_\mathrm{ML}^{1/2}k_\mathrm{d}^{1/2}}&\left\{(s+l)^{1/2}d_\mathrm{r}\right\}\Big\{s^{1/2}\Big[(d_-+d_\mathrm{r})(d_++d_\mathrm{r})^{1/2}\\&-(d_--d_\mathrm{r})(d_+-d_\mathrm{r})^{1/2}\Big]+2\theta\xi k_\mathrm{d}^{1/2}\left(d_+^2-d_\mathrm{r}^2\right)^{1/2}d_\mathrm{r}\Big\}^{-1}\end{aligned} \tag{24}$$

where

$$l=k_\mathrm{d}(1+K') \tag{25}$$

Analytical inversion of eqn. (24) to the time domain is possible only in some limiting cases. Therefore numerical inversion was carried out according to the

TABLE 1

Calculated half-wave potential shifts $(-(nF/RT)\,\Delta E_{1/2}, t)$ (a) from digital simulation [14], using different step sizes, and (b) from inversion of eqn. (24). $K' = 1$, $\epsilon = 0.1$, $k_d = 1$ s^{-1}

t/s	(a)			(b)
	10^3 steps	10^4 steps	10^5 steps	
0.01	0.00944	0.00971	0.00980	0.00977
0.125	0.00998	0.10250	0.10337	0.10364
0.25	0.17074	0.17516	0.17658	0.17703
0.5	0.26421	0.27069	0.27277	0.27339
1	0.36023	0.36854	0.37121	0.37249
2	0.42537	0.43359	0.43622	0.43742
4	0.43447	0.43956	0.44102	0.44165
8	0.41551	0.41763	0.41811	0.41828
16	0.40348	0.40474	0.40470	0.40504
32	0.39816	0.39915	0.39931	0.39935
64	0.39569	0.39657	0.39669	0.39759
128	0.39451	0.39533	0.39543	0.39550

procedure described before [1]. The normalized current parameter Φ is again defined as

$$\Phi(E, t) = \frac{(\pi D_M t)^{1/2}}{c_T^*} L^{-1}\{(\mathrm{d}\bar{c}_M/\mathrm{d}x)_{x=0}\} \tag{26}$$

where $c_T^* = c_M^* + c_{ML}^*$ and L^{-1} denotes the inverse Laplace transform.

Using eqns. (24) and (26), $E_{1/2}$ was calculated as a function of time from

$$\Phi(E_{1/2}, t) - \tfrac{1}{2}\Phi_l(t) = 0 \tag{27}$$

where $\Phi_l(t)$ represents the normalized limiting current. The root of eqn. (27) was obtained using the Regula Falsi method, which is suitable for the present problem [11] and is available as the FORTRAN subroutine ZFALSE in the IMSL library [12].

In Table 1, some results are presented and compared with data obtained by calculations according to the explicit finite difference method [13,14]. The shift of $E_{1/2}$ is calculated with respect to $E_{1/2}$ for M only, which is given by the well-known equation [15]

$$E_{1/2}^{M} = E^\circ - (RT/nF) \ln \xi \tag{28}$$

The agreement between the two approaches is satisfactory provided the time steps in the finite difference scheme are sufficiently small. It is obvious that with an increasing number of time steps in the finite difference calculation, the results approach the data obtained by numerical inversion of eqn. (24), which illustrates the correctness of the latter. The advantage of the numerical inversion procedure has already been outlined [1] and is even more severe in this case because the Regula Falsi routine requires several evaluations of $\Phi(E, t)$ for solution of eqn. (27) with the desired accuracy.

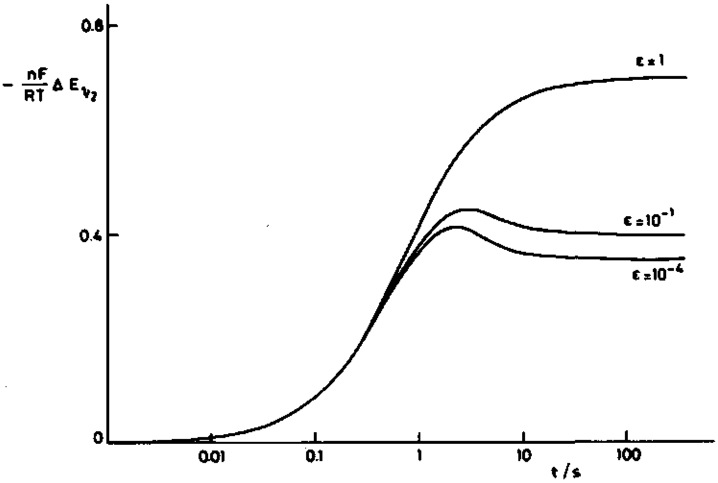

Fig. 1. Half-wave potential shift $\Delta E_{1/2}$ as a function of time for different values of ϵ. $K' = 1$, $k_d = 1$ s^{-1}.

In Figs. 1 and 2 the shift of $E_{1/2}$ is plotted as a function of time for various values of ϵ and K', respectively. The similarities with the time dependence of Φ_1 are striking. For very small values of t, $\Delta E_{1/2}$ is practically zero. Here, the system is in the static regime, where only free M is involved [2]. For very large values of t, the specific examples of Figs. 1 and 2 correspond to labile behaviour. Then $\Delta E_{1/2}$ is independent of t, as will be discussed further below.

The maximum in the $\Delta E_{1/2}$, t plots, typical for semi-dynamic behaviour and $\epsilon < 1$, is related to a discrepancy between the depletion layers of M and ML. As was pointed out in Part II [2], the depletion layer of ML develops more slowly than that

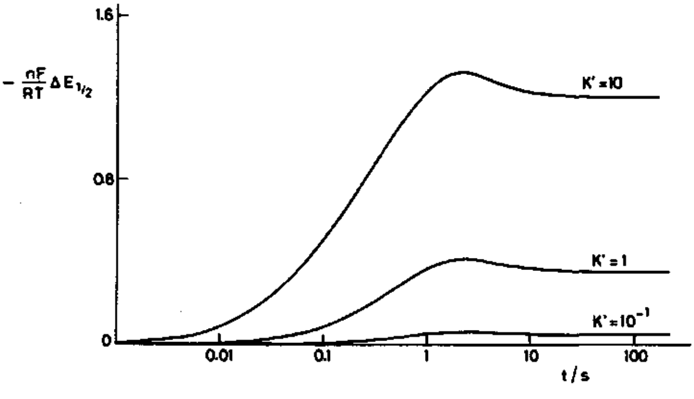

Fig. 2. $\Delta E_{1/2}$ as a function of time for different values of K'. $\epsilon = 10^{-4}$, $k_d = 1$ s^{-1}.

of M if $\epsilon < 1$, and consequently there exist local excesses of ML compared to the equilibrium values. The striking consequence is that, before reaching the final situation of a joint mean diffusion layer, $E_{1/2}$ is shifted towards an even more negative value.

In a considerable part of the semi-dynamic regime, $\Delta E_{1/2}$ is hardly influenced by ϵ. Here, c_{M} close to the electrode is determined mainly by diffusion of M and dissociation of ML, association of M with L and diffusion of ML still being of minor importance [2].

SOME LIMITING CASES

(1) The short time limit ($s \to \infty$)

If s is so large that

$$\frac{s}{k_{\mathrm{a}}'},\ \frac{s}{k_{\mathrm{d}}} \gg 1 \tag{29}$$

then the system behaves statically [2] and eqn. (24) simplifies to

$$(\mathrm{d}\bar{c}_{\mathrm{M}}/\mathrm{d}x)_{x=0} = c_{\mathrm{M}}^{*}/(D_{\mathrm{M}}s)^{1/2}(1+\theta\xi) \tag{30}$$

which leads to the well-known diffusion-controlled current–potential relation for M unperturbed by chemical kinetics:

$$i(t)/nF = D_{\mathrm{M}}^{1/2}c_{\mathrm{M}}^{*}/(\pi t)^{1/2}(1+\theta\xi) \tag{31}$$

where i is the current density.

(2) The long time limit ($s \to 0$)

If s is so small that:

$$\frac{s}{k_{\mathrm{a}}'},\ \frac{s}{k_{\mathrm{d}}} \ll 1 \tag{32}$$

then the system behaves dynamically and eqn. (24) reduces to

$$\left(\frac{\mathrm{d}\bar{c}_{\mathrm{M}}}{\mathrm{d}x}\right)_{x=0} = \frac{c_{\mathrm{M}}^{*}k_{\mathrm{d}}^{1/2}\epsilon^{1/2}(\epsilon^{-1}+K')^{3/2}}{D_{\mathrm{ML}}^{1/2}K'}\,\frac{1}{s^{1/2}\left[s^{1/2}+(1+P)\Lambda\right]} \tag{33}$$

where

$$P = \theta\xi\left[(1+\epsilon K')(1+K')\right]^{1/2} \tag{34}$$

and

$$\Lambda = k_{\mathrm{d}}^{1/2}\epsilon^{-1/2}(\epsilon^{-1}+K')/K'(1+K')^{1/2} \tag{35}$$

After transformation to the time domain, this yields the current–potential relation for a dynamic system:

$$\Phi(E,\, t) = \frac{(\pi k_{\mathrm{d}}t)^{1/2}(\epsilon^{-1}+K')^{3/2}}{K'(1+K')}\,\exp\left[(1+P)^{2}\Lambda^{2}t\right]\,\mathrm{erfc}\left[(1+P)\Lambda t^{1/2}\right] \tag{36}$$

To obtain $E_{1/2}$ for this type of system, eqn. (36) is substituted into eqn. (27) which yields

$$\exp\left[(1+P_{1/2})^2\Lambda^2 t\right] \operatorname{erfc}\left[(1+P_{1/2})\Lambda t^{1/2}\right] = \tfrac{1}{2}\exp[\Lambda^2 t] \operatorname{erfc}[\Lambda t^{1/2}] \tag{37}$$

Using the approximated inverse function of $\pi^{1/2} y \exp(y^2)\operatorname{erfc}(y)$ derived by Oldham and Parry [16]:

$$y = \frac{\phi}{8}\left[\frac{3(7+4\phi^2)}{1-\phi}\right]^{1/2} \tag{38}$$

where $\phi = \pi^{1/2} y \exp(y^2) \operatorname{erfc}(y)$, eqn. (37) can be rearranged to a quadratic equation in $P_{1/2}$ with the root

$$P_{1/2} = -(1+g) + \frac{1}{2}\left\{4(1+g)^2 - 4\left[1 + 2g - \frac{3\pi g^2\gamma^2}{16} + \frac{63\pi^2 g^2\gamma^4}{16^3}\right]\right\}^{1/2} \tag{39}$$

where

$$g = 16^2/(12\pi^{3/2}\gamma^3\Lambda t^{1/2}) \tag{40}$$

and

$$\gamma = \exp(\Lambda^2 t)\operatorname{erfc}(\Lambda t^{1/2}) \tag{41}$$

The shift of $E_{1/2}$ with respect to $E^{\mathrm{M}}_{1/2}$ is now

$$\begin{aligned}(nF/RT)\,\Delta E_{1/2} &= -\ln(\overline{D}/D_{\mathrm{M}})^{1/2} - \ln(1+K') \\ &\quad + \ln\left[-(1+g) + \tfrac{1}{2}\left\{4(1+g)^2 - 4\left(1 + 2g - \frac{3\pi g^2\gamma^2}{16} + \frac{63\pi^2 g^2\gamma^4}{16^3}\right)\right\}^{1/2}\right]\end{aligned} \tag{42}$$

where $\overline{D}$ is the mean diffusion coefficient defined as

$$\overline{D} = D_{\mathrm{M}}(1+\epsilon K')/(1+K') \tag{43}$$

Both eqns. (36) and (42) can be considerably simplified under conditions of lability or non-lability, as will be discussed below.

(2a) The labile case ($\Lambda t^{1/2} \gg 1$)

If $\Lambda t^{1/2} \gg 1$, then

$$\exp\left[(1+P)^2\Lambda^2 t\right]\operatorname{erfc}\left[(1+P)\Lambda t^{1/2}\right] \sim \left[\pi^{1/2}(1+P)\Lambda t^{1/2}\right]^{-1} \tag{44}$$

so that eqn. (36) reduces to

$$\Phi(E,t) = \frac{k_{\mathrm{d}}^{1/2}(\epsilon^{-1}+K')^{3/2}}{K'(1+K')(1+P)\Lambda} \tag{45}$$

which can also be written as

$$\Phi(E,\, t) = \Phi_1(t)/(1+P) \tag{46}$$

Now $\Delta E_{1/2}$ due to complexation is easily found to be

$$(nF/RT)\ \Delta E_{1/2} = -\ln\left(\bar{D}/D_{\mathrm{M}}\right)^{1/2} - \ln(1+K') \tag{47}$$

This result was also obtained by Guidelli and Cozzi [17]. For $\epsilon K' \gg 1$, eqn. (47) reduces to the well-known DeFord–Hume equation [4].

(2b) The non-labile case ($\Lambda t^{1/2} \ll 1$)

If $\Lambda t^{1/2}$ is so small that

$$(1+P)^2 \Lambda^2 t \gg 1 \tag{48}$$

then the experfc function may be approximated by

$$\exp\left[(1+P)^2 \Lambda^2 t\right]\ \mathrm{erfc}\left[(1+P)\Lambda t^{1/2}\right] \sim 1 - \frac{2(1+P)\Lambda t^{1/2}}{\pi^{1/2}} \tag{49}$$

so that eqn. (36) reduces to

$$\Phi(E,\, t) = \frac{(\pi k_{\mathrm{d}} t)^{1/2} (\epsilon^{-1} + K')^{3/2}}{K'(1+K')} \left(1 - \frac{2(1+P)\Lambda t^{1/2}}{\pi^{1/2}}\right) \tag{50}$$

and the solution of eqn. (37) becomes

$$P_{1/2} = -\tfrac{1}{2} + \pi^{1/2}/4\Lambda t^{1/2} \tag{51}$$

from which $\Delta E_{1/2}$ is found to be

$$(nF/RT)\ \Delta E_{1/2} = -\ln\left(\bar{D}/D_{\mathrm{M}}\right)^{1/2} - \ln(1+K') + \ln\left(-\tfrac{1}{2} + \pi^{1/2}/4\Lambda t^{1/2}\right) \tag{52}$$

(3) $D_{ML}/D_M \to 1$

In the case where $D_{\mathrm{ML}} = D_{\mathrm{M}} = D$, eqn. (24) simplifies to

$$\left(\frac{\mathrm{d}\bar{c}_{\mathrm{M}}}{\mathrm{d}x}\right)_{x=0} = \frac{(1+K')c_{\mathrm{M}}^{*}}{D^{1/2}} \frac{(s+l)^{1/2}}{s^{1/2}\left[K' s^{1/2} + (1+P)(s+l)^{1/2}\right]} \tag{53}$$

Using the procedure outlined in Appendix C of Part I, $\Phi(E,\, t)$ is found to be

$$\begin{aligned}\Phi(E,\, t) = \frac{(\pi t)^{1/2}}{K'^2 - (1+P)^2} & \left\{ K' \exp\left(\frac{l+l'}{2} t\right) \sum_{j=1}^{\infty} \frac{\left[\frac{1}{4}(l+l')\right]^{2j} \Gamma(2j+1) t^{2j-1/2}}{\Gamma(2+j+\frac{1}{2})(j!)^2} \right. \\ & \times \left[\left\{ 1 + \frac{(l+l')t}{2(2j+\frac{1}{2})} \right\} {}_1F_1\left(1/2;\, 2j+3/2;\, \frac{l+l'}{2} t\right) \right. \\ & \left. + \frac{(l+l')t}{4(2j+5/2)(2j+3/2)}\, {}_1F_1\left(1/2;\, 2j+5/2;\, \frac{l+l'}{2} t\right) \right] \\ & - \frac{(1+P)}{\pi^{1/2}} \left[(t^{-1/2} + 2lt^{1/2})\, {}_1F_1(1;\, 3/2;\, l't) \right. \\ & \left. \left. + \frac{4l't^{1/2}}{3}\, {}_1F_1(2;\, 5/2;\, l't) \right] \right\} \end{aligned} \tag{54}$$

where l' is now defined as

$$l' = l/\left(K'^2 - (1+P)^2\right) \tag{55}$$

The complexity of eqn. (54) makes it impossible to derive an analytical expression for $E_{1/2}$ in this case. However, the evaluation of $\Delta E_{1/2}$ is easily performed with the aid of a simple numerical procedure, as discussed before.

REFERENCES

1 H.G. de Jong, H.P. van Leeuwen and K. Holub, J. Electroanal. Chem., 234 (1987) 1.
2 H.G. de Jong and H.P. van Leeuwen, J. Electroanal. Chem., 234 (1987) 17.
3 J. Heyrovský and D. Ilkovič, Collect. Czech. Chem. Commun., 7 (1935) 198.
4 D.D. DeFord and D.N. Hume, J. Am. Chem. Soc., 73 (1951) 5321.
5 H. Matsuda and Y. Ayabe, Bull. Chem. Soc. Jpn., 29 (1956) 134.
6 C. Nishihara and H. Matsuda, J. Electroanal. Chem., 51 (1974) 287.
7 H. Matsuda, J. Electroanal. Chem., 56 (1974) 165.
8 J. Galvez, A. Serna, A. Molina and D. Marin, J. Electroanal. Chem., 102 (1979) 277.
9 J. Galvez, C. Serna, A. Molina and A. Serna, J. Electroanal. Chem., 115 (1980) 1.
10 M. Lovrič and I. Ružić, J. Electroanal. Chem., 146 (1983) 253.
11 J. Stoer and R. Bulirsch, Introduction to Numerical Analysis, Springer, New York, 1980.
12 IMSL Library, edition 9.2, IMSL, Houston, 1984.
13 S.W. Feldberg in A.J. Bard (Ed.), Electroanalytical Chemistry, Vol. 3, Marcel Dekker, New York, 1969, pp. 199–296.
14 J.T. Maloy in P.T. Kissinger and W.R. Heineman (Eds.), Laboratory Techniques in Electroanalytical Chemistry, Marcel Dekker, New York, 1984, pp. 417–461.
15 A.J. Bard and L.R. Faulkner, Electrochemical Methods, Wiley, New York, 1980.
16 K.B. Oldham and E.P. Parry, Anal. Chem., 40 (1968) 65.
17 R. Guidelli and D. Cozzi, J. Phys. Chem., 71 (1967) 3027.

CHAPTER 5

PULSE POLAROGRAPHIC SPECIATION OF HEAVY METAL/POLYELECTROLYTE SYSTEMS

INTRODUCTION

In the preceding chapters a theoretical treatment for the voltammetry of complex systems of species with different diffusion coefficients was given. Equations for the limiting current and the half-wave potential could be derived in the Laplace domain. These equations are rigorous with respect to the values of the diffusion coefficients of the species and the values of the complex association/dissociation rate constants. The equations are valid for a stationary planar electrode and an excess of ligand. In principle these equations are the basic tools to solve voltammetric speciation problems.

In earlier work [1] we analyzed voltammetric data of heavy metal/polyelectrolyte systems using the mean diffusion coefficient concept, assuming labile behaviour of the complexes involved. This assumption was justified by the observation that for systems for which the current transient was measured, the Cottrell plots were linear and the half-wave potential was independent of time. However, in certain cases there was a pronounced difference between stability constants calculated from limiting current data and that from half-wave potential shifts. Furthermore, the calculation of stability constants under the assumption of lability completely failed for the Pb/PAA system [2]. A general problem in the exploitation of most of the existing experimental data is that the condition of large excess of ligand, as required by the present theory, is not fulfilled. The magnitude of the ensuing error in the evaluation of the complex stability constant is completely unknown.

The aim of this chapter is to reconsider the treatment of earlier data in order to assess the correctness of the evaluations and where necessary to extend or modify the interpretation of these data using the newly developed theory.

PROCEDURE

The theory developed in the preceding chapters was concerned with a simple complexation scheme in which the free metal ion (M) associates with the ligand (L) to form the complex (ML)

$$M + L \underset{k_d}{\overset{k_a}{\rightleftharpoons}} ML \qquad (1)$$

with

$$K = c_{ML}/c_M c_L \qquad (2)$$

where c_M, c_{ML} and c_L denote the concentrations of M,ML and L respectively and k_a and k_d are the association and dissociation rate constants. When a large excess of ligand is present, the association reaction becomes pseudo first-order with rate constant

$$k_a' = k_a c_L \qquad (3)$$

and the corresponding stability constant then is

$$K' = k_a'/k_d \qquad (4)$$

In chapter 3, the speciation of labile and inert metal complex systems was explained and shown to be straightforwardly. If the system is neither labile nor inert one is faced with determining k_a' and k_d in order to solve the speciation problem. A possible practical procedure would be to record voltammograms of solutions with and without L and to determine the values of Φ_ℓ, the normalized limiting current, and $\Delta E_{\frac{1}{2}}$, the half-wave potential shift. The limiting current is normalized in such a way that it equals 1 if all of the present metal diffuses to the electrode with a diffusion coefficient equal to that of M (chapter 2). The half-wave potential shift is measured relative to the half-wave potential of pure M (chapter 4). Now with the experimental values of Φ_ℓ and $\Delta E_{\frac{1}{2}}$, denoted as $\Phi_\ell(\exp)$ and $\Delta E_{\frac{1}{2}}(\exp)$ respectively, a set of two simultaneous equations can be constructed

$$\Phi_\ell(K';k_d;\varepsilon;t) - \Phi_\ell(\exp) = 0 \qquad (5)$$

$$\Delta E_{\frac{1}{2}}(K';k_d;\varepsilon;t) - \Delta E_{\frac{1}{2}}(\exp) = 0 \qquad (6)$$

where $\Phi_\ell(K';k_d;\varepsilon;t)$ is the theoretical function described by eqn. (18) of chapter 2, $\Delta E_{\frac{1}{2}}(K';k_d;\varepsilon;t)$ is the root of eqn. (27) of chapter 4, ε is the ratio of the diffusion coefficients of ML and M (see chapter 2) and t is the pulse time. In order to solve this set of equations a FORTRAN program was developed. It uses K', k_d, ε and t as input parameters. The values of ε and t are usually known, K' and k_d must be guessed. The program contains the subroutine ZCNT from the IMSL library [3] and this enables the solution of the two non-linear equations for K' and k_d by an iterative procedure which uses the guessed values of both parameters as starting values. The program also incorporates the subroutine FLINV, again from the IMSL library [3], which enables inversion of Laplace transformed functions to the time domain. Here it is used to calculate the current from eqn. (24) of chapter 4 as a function of K', k_d, ε, t and the applied potential.

EXPERIMENTAL

The polyelectrolytes employed were polyacrylicacid (PAA) and polymethacrylic acid (PMA). These polyacids are fairly well-behaved in aqueous solution and their metal-binding properties are appropriate for the present purposes. They were obtained from Polysciences and BDH, respectively. Average molar masses were 26,000 g for the PMA and 50,000 g for the PAA sample used. Experiments were carried out at a concentration level of about 2.5 mM acidic groups. The exact concentrations of the polyacid solutions were determined by conductometric titration. The charge of the polyacid species is related to the degree of neutralization (α_n), a parameter determined by the number of carboxylic groups which have been deprotonated (by adding KOH). Cadmium(II) nitrate (Baker), zinc(II) nitrate (Baker), lead(II)nitrate (BDH) and potassium nitrate (Baker) were of p.a. quality. All the experiments were carried out at 25 °C.

The polarograms were obtained using a modified PAR 174A polarograph in the normal pulse mode. The modification allows variation of the effective pulse duration t. The applied t values ranged from 14.5 ms to 175 ms. The PAR/EG&G model 303, in the repeating mode, served as the indicator electrode. Unless indicated otherwise, the drop period was 1 s. Potentials are referred to the $Ag/AgCl/KCl_{sat}$ electrode. Traces of oxygen were removed from the polarographic cell by passing purified N_2 through the solution for about 10 min.

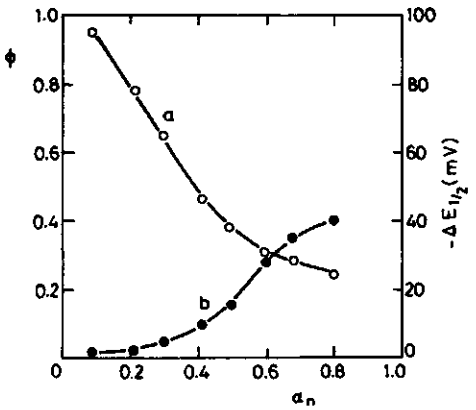

FIGURE 1 : Experimental results for the Zn/PMA system as a function of α_n. a. $\Phi_\ell(\exp)$; b. $\Delta E_{\frac{1}{2}}(\exp)$. [Zn]/[polyacid]=0.2; $[KNO_3]=5\times10^{-2}$ M; $E_1=-900$ mV; $t=0.175$ s (from ref. 1).

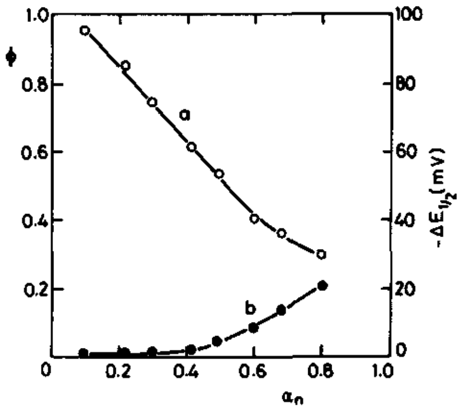

FIGURE 2 : Experimental results for the Cd/PMA system as a function of α_n a. $\Phi_\ell(\exp)$; b. $\Delta E_{\frac{1}{2}}(\exp)$. [Cd]/[polyacid]=0.2; $[KNO_3]=5\times10^{-2}$ M; $E_1=-500$ mV; $t=0.175$ s (from ref. 1).

RESULTS AND DISCUSSION

The Zn/PMA system

In Fig.1 $\Phi_\ell(\exp)$ and $\Delta E_{\frac{1}{2}}(\exp)$ are plotted as a function of the degree of neutralization for the Zn/PMA system. Measurements of complete transients revealed that the limiting current varies linearly with $t^{-\frac{1}{2}}$ and the half-wave potential shift is independent of the pulse time. These observations indicate labile behaviour of this system under the present conditions. Calculation of K values from limiting current and potential data using the equations for the labile limit (e.g. eqn. (16) of ch.3 and eqn.(47) of ch. 4) yielded consistent results (see Fig.3).

The lability criterion which is extensively discussed in chapter 3 reads

$$\Lambda^2 t \gg 1 \tag{7}$$

where

$$\Lambda = \frac{k_d^{\frac{1}{2}}\,\varepsilon^{-\frac{1}{2}}\,(\varepsilon^{-1} + K')}{K'(1 + K')^{\frac{1}{2}}} \tag{8}$$

For the present system and the given experimental conditions ε,t and K' were of the order of magnitude of 10^{-2},10^{-1} s and 10 respectively. This yields for inequality (7) : $k_d \gg 10^{-2}\ s^{-1}$. For the given pulse time, this condition is less severe than the requirements for dynamic behaviour,i.e. $k_a't$ and $k_dt \gg 1$.

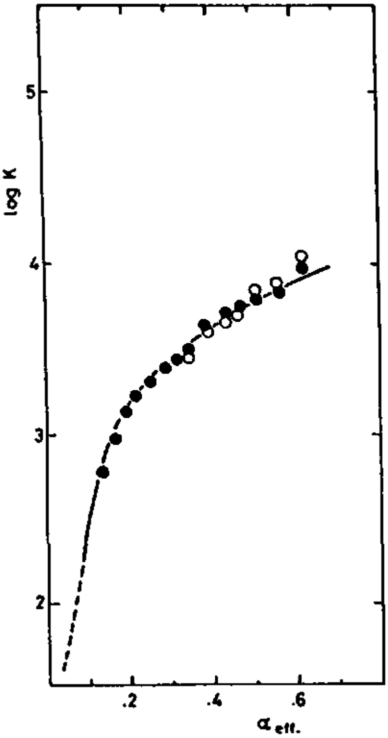

FIGURE 3 : Dependence of log K on α_{eff} for the Zn/PMA system (details see Fig. 1). Curves : from Φ_{ℓ}(exp) data; open symbols : from $\Delta E_{\frac{1}{2}}$(exp) data.

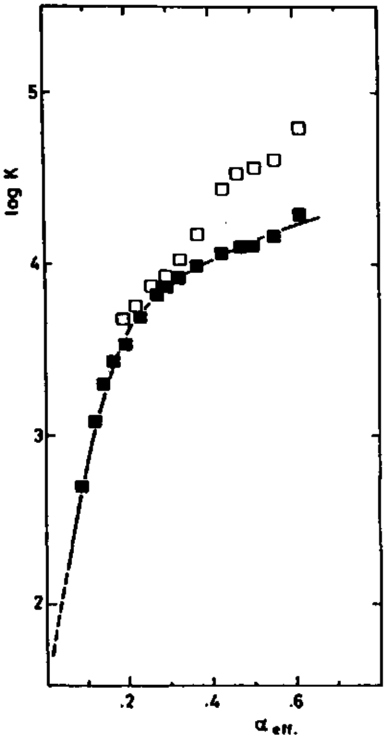

FIGURE 4 : Dependence of log K on α_{eff} for the Cd/PMA system (details see Fig 3). Curves : from Φ_{ℓ}(exp) data; open symbols : from $\Delta E_{\frac{1}{2}}$(exp) data.

It means that for this set of values fulfillment of the dynamic conditions immediately implies lability and consequently that this system cannot be non-labile. In order to estimate a lower limit of k_d, Φ_{ℓ}(exp) and $\Delta E_{\frac{1}{2}}$(exp) are compared with the theoretical values of table I which were obtained by the numerical procedures outlined in the chapters 2 and 4. As a result k_d is found to be at least 10^2 s^{-1} thus proving the labile behaviour of the Zn/PMA system at the present experimental time scale. It further follows that k_a' is at least 10^3 s^{-1}, a value which is in line with the suggestion that the rates of complexation reactions of transititon metal ions are probably determined by the dehydration step for which rate constants in the order of 10^5 s^{-1} may be expected [4,5].

In Fig. 1 one observes unusually strong dependencies of Φ_{ℓ}(exp) and $\Delta E_{\frac{1}{2}}$(exp) on α_n. This is due to an increase of K with increasing α_n, a phenomenon which is typical for polyionic ligands. Due to the increasing charge density on the polyion, the electrostatic contribution to the overall Gibbs free energy of binding increases. The dependence of K on the average spacing between the charged groups on the polyion may be further demonstrated

Table I : Φ_ℓ and $\Delta E_{\frac{1}{2}}$ as a function of k_d. $K'=10$; $\varepsilon=0.01$; $t=0.1$ s.

k_d (s^{-1})	Φ_ℓ	$-nF\Delta E_{\frac{1}{2}}/RT$
0.1	0.09979	0.09043
1	0.1644	0.5072
10	0.3432	1.225
100	0.3260	1.278
1000	0.3171	1.249
10000	0.3163	1.247

by plotting K vs. α_{eff}, the free ligand fraction (see Fig. 3). Satisfactory explanations for these results have been given [2,6,7].

The Cd/PMA system

In Fig. 2 Φ_ℓ(exp) and $\Delta E_{\frac{1}{2}}$(exp) are plotted as a function of α_n for the Cd/PMA system. Analysis of these data assuming lability yielded sets of K values that differed significantly at the higher values of α_{eff} (see Fig. 4). The K values obtained from the half-wave potential data are appreciably higher than those from the limiting current data. For systems which are not labile i.e. dynamic or semi-dynamic, analysis of Φ_ℓ and $\Delta E_{\frac{1}{2}}$ data assuming labile behaviour yields just the opposite picture. To illustrate this Φ_ℓ and $\Delta E_{\frac{1}{2}}$ data are calculated for a semi-dynamic system according to the numerical procedures outlined in chapter 2 and 4 and subsequently analyzed as if it were a labile system. The results of this exercise are presented in table II. Clearly, the K' values obtained from $\Delta E_{\frac{1}{2}}$ are much lower than those evaluated from Φ_ℓ. In both cases the K' values strongly differ from the correct value. These findings suggest that for the Cd/PMA system the homogeneous chemical reaction kinetics cannot account for the observed differences in K' values from $\Delta E_{\frac{1}{2}}$ and Φ_ℓ data, the more so since the simultaneous eqns. (5) and (6) could not be solved for this system.

More detailed experimental work [8] showed a dependence of Φ_ℓ on the initial potential. This strongly indicates adsorption of the metal ion induced

Table II : Calculated Φ_ℓ and $\Delta E_{\frac{1}{2}}$ data for a semi-dynamic system and analysis of these data assuming labile behaviour. ε=0.01; t=0.1 s; k_d=1 s^{-1}.

exact parameters			results of analysis (incorrectly) assuming lability	
K'	Φ_ℓ	$-nF\Delta E_{\frac{1}{2}}/RT$	K'(from Φ_ℓ)	K'(from $\Delta E_{\frac{1}{2}}$)
5	0.239	0.324	20	0.89
10	0.164	0.507	58	1.7
15	0.134	0.636	1.2×10^2	2.5
20	0.116	0.736	2.9×10^2	3.2
25	0.104	0.819	1.2×10^3	4.0

by adsorption of the polymethacrylate in the period prior to pulse application [9]. Adsorption of polymethacrylate complexes occurs especially in the potential region around the potential of zero charge. For Cd(II), with $E_{\frac{1}{2}}$ near -0.6 V, initial potentials are chosen somewhere in this region. In the case of the Zn/PMA system the initial potential was -900 mV. At this potential the electrode carries such a negative charge that polmethacrylate adsorption is prevented by electrostatic repulsion and therefore the data for this system can be consistently analyzed by taking into account homogeneous chemical kinetics only.

The Pb/PAA system

In Fig. 5 Φ_ℓ(exp) and $\Delta E_{\frac{1}{2}}$(exp) are presented as a function of α_n for the Pb/PAA system. These data could not be analyzed on the basis of the assumption of labile behaviour. For example computations with limiting current data yielded negative values for K. By contrast, using the given values for ε and t of 0.023 [2] and 0.175 s respectively, eqns. (5) and (6) could be solved without any problem. For K' and k_d values were found to be of the order of 10^4 and 10^2 s^{-1} respectively for the system with $0.6<\alpha_n<0.8$. Thus this particular system seems to have a dynamic nature because $k_a't \approx 2 \times 10^5$ and $k_d t \approx 2 \times 10^1$. The

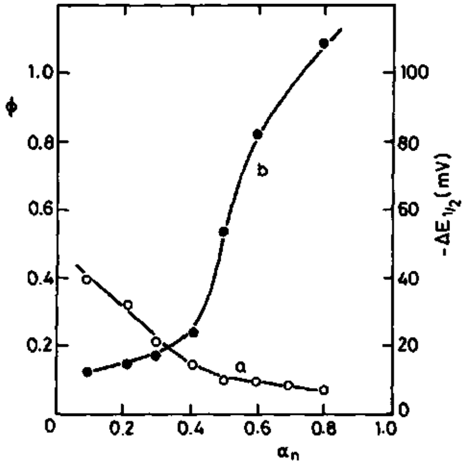

FIGURE 5 : Experimental results for the Pb/PAA system as a function of α_{eff} a. Φ_{ℓ}(exp); b. $\Delta E_{\frac{1}{2}}$(exp). [Pb]/[polyacid]=0.2; $[KNO_3]=5X10^{-2}$ M; E_i=-250 mV; t=0.175 s (from ref. 2).

lability parameter $\Lambda t^{\frac{1}{2}}$ can be calculated to be of the order of 10^{-1} which indicates that the Pb/PAA system under the given conditions is an example of a system which is dynamic but not labile. This means that the measured currents are strongly influenced by the association/dissociation kinetics in the solution. In order to determine the kinetic parameters more accurately, additional experiments - such as recording complete transients - would be necessary. Furthermore, some reservation should be made because sometimes the lead/polyacrylate system tends to flocculate/precipitate and at the initial potential of -250 mV induced adsorption of the metal ion may also play a role. These aspects would need some more careful experimental verification.

In the data analysis given so far a large excess of ligand was tacitly implied. Actually in the experiments performed here, the largest excess of ligands ($-COO^-$ groups) was about 4 times the total metal concentration. As a first step in tackling this problem, we carried out some digital simulations of the metal flux at the electrode surface taking into account the influence of the actual ligand concentration. As a typical result it was found that even at the lowest metal-to-ligand ratio in the above mentioned experimental data, disregarding the flux of ligands leads to an underestimation of the value of K' by almost 20 %. This clearly demonstrates the approximate character of the results obtained so far and the need of further developing the theoretical investigations to include ligand transport.

CONCLUSIONS

Under the conditions outlined in the experimental section the Zn/PMA system is labile. The K values as evaluated from limiting current and half-wave potential data using the mean diffusion coefficient concept are consistent. For the Cd/PMA system the data analysis using the theory for homogeneous first-order complexation kinetics seems to be disturbed by adsorption of the complex. The Pb/PAA system seems to be dynamic and not labile under the conditions given in the experimental section. In order to solve the remaining problems, experimental work on the time dependence of both the limiting current and the half-wave potential shift shows the best perspective. In this, it could be useful to include reverse pulse polarography in order to eliminate adsorption effects. Theoretical efforts are necessary in the analysis of systems in which there is no excess of ligand. Work in this field is also very important for a correct interpretation of voltammetric metal titrations of environmental samples. Extension of the new rigorous theory to more sensitive methods such as differential pulse polarography and anodic stripping voltammetric techniques is necessary to be able to deal with the low concentration levels of heavy metals encountered in natural samples.

REFERENCES

1. R.M.F.J. Cleven, H.G. de Jong and H.P. van Leeuwen, J.Electroanal.Chem., 202(1986)57.
2. R.M.F.J. Cleven, Ph.D. Thesis, Wageningen, Agricultural University, Wageningen, The Netherlands, 1984.
3. IMSL library edition 9.2, IMSL, Houston, 1984.
4. J. Buffle in H. Sigel (Ed.), Metal Ions in Biological Systems, Vol. 18, Marcel Dekker, New York, 1984, p. 165-221.
5. F. Basolo and R.G. Pearson, Mechanisms of Inorganic Reactions; a Study of Metal Complexes in Solution, John Wiley, New York, 1958.
6. C. Travers and J.A. Marinsky, J.Polym.Sci., 47(1974)285.
7. J.C. Leyte and M. Mandel, J.Polym.Sci. Part A,2(1964)1879.
8. M. Esteban, personal communication.
9. R.M.F.J. Cleven, W.F. Threels and H.P. van Leeuwen., Collect. Czech. Chem. Commun., 46(1981)3027.

Biophysical Chemistry 27 (1987) 173–182
Elsevier

CHAPTER 6

Conductometric analysis of the competition between monovalent and divalent counterions in their interaction with polyelectrolytes

Hans G. de Jong, Johannes Lyklema and Herman P. van Leeuwen
Laboratory for Physical and Colloid Chemistry, Agricultural University, De Dreijen 6, 6703 BC Wageningen, The Netherlands

Received 3 August 1986
Revised manuscript received 10 February 1987
Accepted 16 March 1987

Conductometry; Competitive counterion binding; Alkali polyacrylate; Polyelectrolyte

A procedure is described for the analysis of the conductivity of solutions of anionic polyelectrolytes in which both mono- and divalent counterions are present. The method is based on analysis of the relation between the overall conductivity of the system and the conductivity of the individual monovalent cations which are only electrostatically (non-specifically) bound. The system is described in terms of the two-state approach, implying that the counterions are considered to be either fully bound to the polyion or completely free. The potentialities of the proposed method are explored by studying solutions of alkali polyacrylates with and without added zinc nitrate at several alkali nitrate concentrations. The results give a picture of the composition of the counterionic atmosphere around the polyion in systems with both mono- and divalent counterions present. To a certain degree, the divalent ion Zn(II) was found to be bound quantitatively by the polyion. The composition of the counterionic atmosphere around the polyion was largely independent of alkali nitrate concentration when the latter was present in not too large an excess with respect to both Zn(II) and the charged monomers.

1. Introduction

Conductometry has become an important tool in the analysis of properties of polyelectrolyte solutions [1–5]. The properties which have been studied thus far are the concentration dependence of the conductivity of polycarboxylates [1] and polystyrenesulfonates [2], the temperature dependence of the conductivity of alkali polycarboxylates and the influence of the degree of neutralization [1]. Furthermore, the influence of the nature of the counterion on the conductivity of polyelectrolyte solutions has been studied [1,3,5] and a detailed investigation of the conductivity of alkali polymethacrylates in the presence of the corresponding alkali bromide has been performed [3].

Recently, conductometric titration was suggested as a tool for investigating the interaction of polyelectrolytes with heavy metals [4,6]. Such an approach is promising because of the fairly easy way in which the automation of equipment is achieved. Furthermore, the transport properties of polyelectrolyte solutions are more sensitive to the polymer configuration than the equilibrium properties [2], which means that in principle more information can be obtained from measurements of transport properties than those of equilibrium. In the analysis of Cleven [4], the interpretation remained more or less qualitative.

In another study, calculations of the overall conductivity were given for polysulfonic acids partly neutralized by Mg^{2+} [7]. However, competition between monovalent and divalent counterions in their interaction with the poly acids has not yet been assessed conductometrically nor was the behavior of the bound fractions of the two types of

Correspondence address: H.G. de Jong, Laboratory for Physical and Colloid Chemistry, Agricultural University, De Dreijen 6, 6703 BC Wageningen, The Netherlands.

counterions involved. The present work is aimed at a systematic analysis of the conductivity of mixed-valency counterion-polyelectrolyte systems. This involves the quantification of bound (or free) fractions of the counterions involved, including competition in their interaction with the polyion. Such an analysis is a basic step in the further investigation of these complex systems. The analysis is based on the two-state approach, i.e., counterions are assumed to be found either in some kind of bound state or are entirely free, in the sense that they are not at all influenced by the electric field around the polyion. Such a two-state approach is common in polyelectrolyte theory [7–9]. In this study alkali polyacrylates are chosen as the model systems. They are titrated with zinc nitrate. The results are compared with radioactive counterion tracer diffusion data.

2. Theory

In this section the interpretation of the conductometric titrations of an aqueous polyelectrolyte solution with a solution of a divalent metal salt in systems with or without added 1 : 1 salt is described. First, the case in the absence of added 1 : 1 salt will be treated.

2.1. *Conductivity of mixed-valency counterion-polyelectrolyte solutions*

According to the two-state approximation [8], the specific conductivity of a polyelectrolyte solution, which consists of negatively charged polyions together with several types of counterions and co-ions, may be written as:

$$\kappa = \sum_i f_i \lambda_i^\circ C_i + \sum_j (\lambda_-)_j (C_-)_j + f_\mathrm{p} \lambda_\mathrm{p} C_\mathrm{p} \tag{1}$$

where

C_i, C_p and $(C_-)_j$ denote the total concentrations of counterions of type i, deprotonated groups on the polyion and co-ions of type j, respectively;

λ_i° the molar conductivity of counterions of type i in pure solvent;

λ_p and $(\lambda_-)_j$ the molar conductivities of the polyion (per mol deprotonated monomers) and co-ions of type j, respectively;

f_i and f_p the fractions of conductometrically free counterions [6,10] of type i and deprotonated groups, respectively; and

$f_i \lambda_i^\circ C_i$ and $(\lambda_-)_j (C_-)_j$ the contributions to the total conductivity of counterions of type i and co-ions of type j, respectively.

Bound ions are defined as ions having the same mobility as the polyion. Upon binding of a counterion, the contributions to the overall conductivity of both the bound ion and an electrically equivalent amount of deprotonated monomers are annihilated.

The relation between θ_i, the number of bound counterions per deprotonated monomer, and f_i reads:

$$\theta_i = \frac{z_i (1 - f_i) C_i}{C_\mathrm{p}} \tag{2}$$

and f_p is then written as:

$$f_\mathrm{p} = 1 - \sum_i \theta_i \tag{3}$$

Applying eqs. 1–3 to the titration of a salt-free polyelectrolyte solution with a 2 : 1 salt, the specific conductivity of the mixture may, for any stage of the titration, be written as:

$$\kappa(C_2) = f_1(\lambda_1^\circ + \lambda_p) C_1 + \left[f_2 \lambda_2^\circ - 2(1 - f_2)\lambda_\mathrm{p} \right] C_2 + \lambda_- C_- \tag{4}$$

The subscripts 1 and 2 refer to monovalent and divalent counterions, respectively. Note that in the salt-free case $C_\mathrm{p} = C_1$. The contributions of H^+ and OH^- to the total conductivity are ignored, because under the conditions of our experiments with poly (acrylic acid), (PAA) their concentrations were negligible. The molar conductivity of the solution may be represented as:

$$\Lambda = \kappa(C_2)/(C_\mathrm{p} + C_-) \tag{5}$$

2.2. *The conductivity excess function*

The conductivity excess was shown to be a suitable parameter for representing conductometric titration data [4]. It is defined as the difference between the specific conductivity of a metal/polyelectrolyte system and the sum of the conductivities of the metal salt and polyelectrolyte solution before mixing. For the case of *titration* with a divalent electrolyte:

$$\Delta\kappa_{\mathrm{T}} = -\left\{\kappa(C_2) - \left[\kappa(C_2=0) + \kappa_{\mathrm{bl}}(C_2)\right]\right\} \qquad (6)$$

The sign is chosen for convenience such that association phenomena give rise to a positive $\Delta\kappa_{\mathrm{T}}$. Here, $\kappa_{\mathrm{bl}}(C_2)$ is the specific conductivity of a solution of the 2 : 1 salt:

$$\kappa_{\mathrm{bl}}(C_2) = \lambda_2^\circ C_2 + \lambda_-^\circ C_- \qquad (7)$$

In eq. 6, $\kappa(C_2=0)$ represents the specific conductivity of the polyelectrolyte solution without added 2 : 1 salt. It is equal to:

$$\kappa(C_2=0) = f_{1,0}(\lambda_1^\circ + \lambda_{\mathrm{p}})C_1 \qquad (8)$$

where $f_{1,0}$ is the fraction of conductometrically free monovalent counterions in the polyelectrolyte solution without added 2 : 1 salt. To a good approximation λ_- is not influenced by the electric field around the polyion [3]. Combination of eqs. 4 and 6–8 yields:

$$\Delta\kappa_{\mathrm{T}} = (f_{1,0} - f_1)(\lambda_1^\circ + \lambda_{\mathrm{p}})C_1 + (\lambda_2^\circ + 2\lambda_{\mathrm{p}})(1 - f_2)C_2 \qquad (9)$$

Generally, polyanions prefer binding of divalent over monovalent counterions [11]. This allows one to interpret the first term on the right-hand side of eq. 9 as the conductivity gain due to the release of bound monovalent ions by binding of divalent ions. The second term represents the conductivity loss due to divalent counterion binding. It is obvious that the parameter f_1 depends on C_2. For a complete analysis of the titration data in terms of conductivity excesses, it is necessary to determine the relationship between these two parameters. Furthermore, at every point of the titration λ_{p} must be known.

2.3. Determination of f_1 and λ_p in systems with and without added 1 : 1 salt

From eq. 8 a linear relationship is expected between the molar conductivity of a polyelectrolyte and λ_1° if $f_{1,0}$ is a constant. This is the case if, upon a change in the nature of the monovalent cation, its extent of binding remains unaltered. This situation is expected to occur if the counterions are purely electrostatically (i.e., non-specifically) bound. The linearity sought has been shown to apply for Li, Na and K polyacrylates at the millimolar level [3]. Therefore, in that case it is possible to evaluate $f_{1,0}$ together with λ_{p} from a plot of Λ vs. λ_1° for Li, Na and K polycarboxylate solutions. The slope and intercept of the straight line obtained in this way equal $f_{1,0}$ and $f_{1,0}\lambda_{\mathrm{p}}$, respectively.

When the competition between the alkali metal counterions and the divalent counterion is not specific and λ_{p} remains unaltered (see section 4.2), the plot of Λ vs. λ_1° will remain linear as in the absence of the divalent counterion. Therefore, the procedure described above remains applicable and f_1 can be determined from the slope of the plot of Λ vs. λ_1°.

In the presence of an added 1 : 1 salt essentially the same procedure can be used when the additivity rule applies. According to this rule, the overall specific conductivity of a polyelectrolyte solution may be written as the sum of independent contributions of the specific conductivities of the added 1 : 1 salt and the polyelectrolyte system [3]. The additivity rule was found to be valid for several properties of polyelectrolyte solutions [3,12,13]. The specific conductivity of the polyelectrolyte system is then:

$$\kappa = \kappa_{\mathrm{total}} - \kappa_{\mathrm{a}} \qquad (10)$$

where κ_{a} is the specific conductivity of the added 1 : 1 salt. From κ, the molar conductivity of the polyelectrolyte system is easily calculated and the relation between Λ and λ_1° is analyzed. In this case the slope is equal to $(1-\theta_1)$ rather than to f_1. For a salt-free system $(1-\theta_1)$ is of course equal to f_1 according to eq. 3.

3. Experimental

Conductivity measurements were performed with a Wayne Kerr B 905 automatic precision bridge, equipped with and IEEE interface allowing computer control. The conductometric cell was a WTW model LTA 01 with a cell constant of 0.109 cm^{-1}. The cell constant was periodically calibrated. All conductivity measurements were performed at a frequency of 10 kHz. A Metrohm type 655 automatic buret was used to add 50- or 100-µl aliquots of 0.05 M $Zn(NO_3)_2$ solution to 50 ml of sample solution. The titration was controlled by an HP 85 A (Hewlett Packard) personal computer programmed with BASIC. The temperature inside the titration vessel was maintained at $25.00 \pm 0.02°C$ by a Julabo F10 thermostat. The automatic buret and titration vessel were kept in an air temperature controlled environment maintained at $25.0 \pm 0.5°C$ with a home-made air thermostat. Prior to measurements, samples were stirred for about 1 h to achieve thermal equilibrium, while purging with CO_2-free, water-saturated N_2 at 25°C. After every addition the sample was stirred and purged with N_2 for about 5 min. During the actual measurement N_2 was passed over the solution. All samples were prepared using demineralized tap water, produced by a Millipore Super-Q reverse osmosis system. After removing CO_2, the conductivity of this water never exceeded 0.6 µS cm^{-1}.

All chemicals used were of analytical grade. Polyacrylic acid (PAA, average molecular mass 230 kDa) was obtained from BDH Chemicals and used without further treatment.

For fully deprotonated PAA, the structural charge density parameter ξ, which is defined as the ratio between the Bjerrum length (l_B) and the average distance between the charged monomers b, under the present experimental conditions is $\xi = l_B/b = 2.85$. For a particular degree of neutralization α_n, ξ becomes $\alpha_n l_B/b$.

Solutions of alkali polyacrylates were prepared

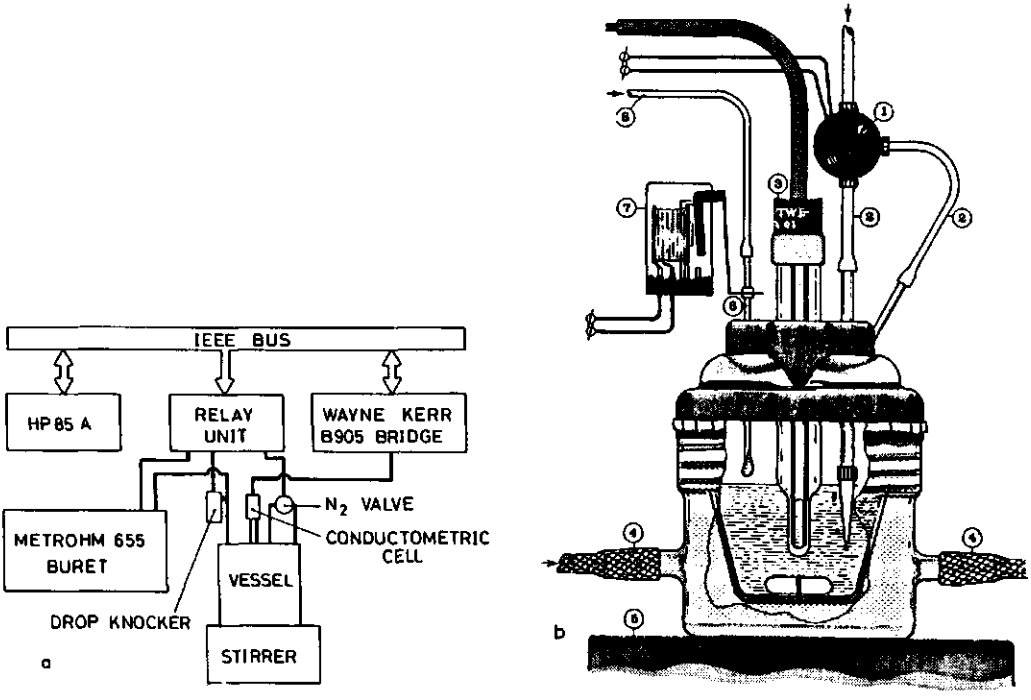

Fig. 1. (a) Block diagram of the experimental set-up. (b) Close-up of the titration vessel. 1, nitrogen valve; 2, nitrogen outlets; 3, conductometric cell; 4, thermostat connections; 5, stirrer; 6, injection needle; 7, drop-knocker; 8, inlet titration solution.

by neutralizing the poly acid with the appropriate hydroxide solution to the desired degree of neutralization.

The set-up is shown schematically in fig. 1a and b. The precision of the measured conductivity steps achieved with this system was typically 0.2% for 50- and 100-μl additions of 0.05 M $Zn(NO_3)_2$ to water on two consecutive days.

4. Results and discussion

4.1. Conductance of alkali polyacrylate solutions

In fig. 2 plots are shown of the molar conductivity of several alkali polyacrylates vs. that of the alkali ions in pure solvent at different concentrations of Zn(II). The linear relationship between Λ and λ_1° is obvious at all Zn(II) concentrations. This means that the non-specific nature of the interaction of alkali metal ions and the polyacrylate anion, as previously found by Eisenberg [1] and Van der Drift [3] for the polymethacrylates, persists during their competition with Zn^{2+} for binding by the polyion. Using eq. 5 this result enables one to calculate f_1 at any stage of titration of alkali polyacrylate solutions with a zinc salt solution. The f_1 value in blank alkali polyacrylate solution, with [PAA] = 2.50 mM and $\alpha_n = 0.8$ was found to be 0.47 ± 0.02 which is in excellent agreement with the results obtained from radioactive tracer diffusion measurements, performed by Ander and Kardan [13]. These results are in accordance with theoretical expectations [7,8]. It may be noted that with this f_1 value the net charge density parameter ξ_{net} is not far from unity, in accordance with Manning's predictions [11].

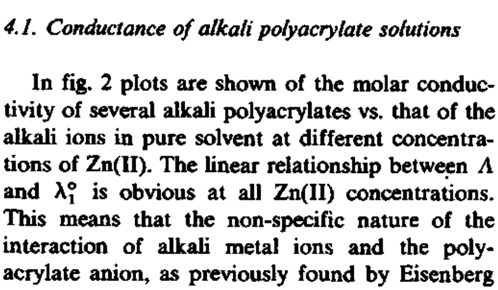

Fig. 2. Plot of the molar conductivity of alkali polyacrylate solutions at the indicated zinc concentrations vs. molar conductivity of the corresponding monovalent counterion.

As outlined in section 2, λ_p can be evaluated from the Λ vs. λ_1° plot. This procedure yields $\lambda_p = 30 \pm 5$ S cm^2 mol^{-1} for a solution with [PAA] = 2.50 mM and $\alpha_n = 0.8$. Anticipating the analysis of the relationship between f_1 and C_2/C_1 it was found that an alternative procedure is available, yielding a more precise value for λ_p: extrapolation of f_1 vs. C_2/C_1 (fig. 4) to zero yielded $f_{1,0} = 0.469 \pm 0.005$. Using this value, λ_p was calculated from the molar conductivity of Li, Na and K polyacrylate solutions. An average value of 31.1 ± 0.8 S cm^2 mol^{-1} was obtained. This procedure was used in all other evaluations of λ_p.

4.2. Behavior of λ_p

In table 1, λ_p values are listed for different degrees of neutralization. An increase in λ_p with decreasing α_n is observed. Qualitatively the same behavior was found for polymethacrylates [3] and carboxymethylated hydroxyethylcellulose [14]. At relatively high salt concentrations (0.1 M NaCl) this trend was reversed for sodium polyacrylate as

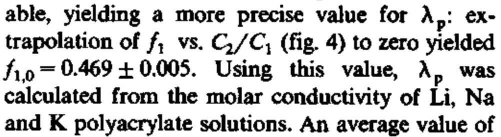

Fig. 3. Conductivity excess curves of three alkali polyacrylate solutions as a function of the concentration of Zn(II). Standard deviation of $\Delta\kappa_T$ values was typically about 0.4 μS cm^{-1}.

reported by Noda et al. [15]. Probably conformational aspects play a role in this matter in the sense that the frictional coefficient of the polyion is dependent on the charge density. In the salt-free case, highly charged polyions may have a cylindrical shape, whereas lower charged polyions have a more compact worm-like chain conformation [16] with a lower frictional coefficient. The λ_p data in table 1, which will be further discussed below, suggest that the change in frictional drag dominates the change in electrical force on the polyion when changing the charge density. When a large amount of a 1 : 1 salt is added, the dimensions of the polyion become smaller [16] and variation in frictional drag is not as important as in the salt-free case, which probably accounts for the observed differences. For $\alpha_n = 0.8$, the dependence of λ_p on concentration of added 1 : 1 salt is presented in table 2. A large decrease in λ_p with increasing concentration of added 1 : 1 salt is observed. The same trend, although less dramatically, was found for alkali polymethacrylates [3].

Fig. 3 shows some typical conductivity excess curves for alkali polyacrylates with a highly charged polyion. It appears to be a general experience that the first data points of the conductivity excess curves form a straight line (statistics for Li polyacrylate, first five data points $R^2 = 1.000$; $F = 10\,899$). The same is true for certain data points for higher concentrations of added zinc nitrate (statistical data for Li polyacrylate, next four data points $R^2 = 1.000$; $F = 6485$. Finally, the curves become horizontal. The linear dependence of the conductivity excess on C_2 implies that $\Delta\kappa_T$ is independent of λ_p. There are two circumstances in which this independence could be established. The first is if $(f_{1,0} - f_1)C_1 = -2(1 - f_2)C_2$, which is the case when, upon binding of one Zn^{2+}, two bound monovalent ions are released. The second option is that λ_p is constant during titration. Analysis of data on the basis of the first assumption yields values for $1 - f_2$ that systematically were in the range 1.2–1.5, which is clearly impossible. Therefore, it is concluded that λ_p is essentially constant during titration. It is well known from theory that λ_p may be dependent on λ_c° [17,18]. From the expression for the electric mobility of a polyion derived by Imai and Iwasa [18], using a value of the order of 10^{12} kg mol^{-1} s^{-1} for the frictional coefficients of counterions (calculated from diffusion coefficients [19]) and a frictional coefficient of the uncharged polyion within the range 10^{14}–10^{15} kg mol^{-1} s^{-1} (ref. 14 and unpublished results of this laboratory), the electric mobility of the polyion is indeed found to be essentially independent of the type of counterion.

If it is true that in the course of the titration under the present experimental conditions no change in dimensions occurs, the contribution to the electric mobility of an individual charged group on the polyion should not be affected by addition of Zn^{2+}. Thus, if the solvent properties do not change during the titration, the only parameter left to affect the net conductivity of the polyion is its apparent charge. Hence, its net conductivity for any point during the titration is f_p times the λ_p found in blank polyelectrolyte solutions. Therefore, λ_p in eqs. 2,4 and 9 is the λ_p calculated from blank polyelectrolyte solutions. This reasoning is supported by dynamic light scattering experiments performed by Magdelénat et al. [20] who found a linear decrease in overall mobility of the polyionic species, when titrating Na chondroitin sulfate with Ca^{2+}. This linear decrease indicates that the mobility of the polyionic species is, at least in part of the titration, only dependent on its apparent charge. The same type of behavior of λ_p was tacitly implied by Thibault and Rinaudo [21] in their calculations concerning conductivity data of a polyelectrolyte solution with only divalent counterions present.

Finally, from fig. 3 it is clear that the $\Delta\kappa_T$ curves show a small intercept. Strictly they should pass through the origin. This observation may suggest that during the titration λ_p may be a constant, which is different from the initial value. However, analysis of the intercept in terms of this concept yields a λ_p value which is not significantly different from the starting value. Furthermore, calculation of $1 - f_2$ from the slope of the linear parts of the conductivity excess curves yields the same value as obtained by calculation using the $\Delta\kappa_T$ values point by point. This suggests that the observed intercepts are of incidental nature and do not seriously affect the analysis.

4.3. Analysis of conductivity excess curves

As demonstrated in fig. 3, the conductivity excess curves of the alkali polyacrylates show similar shapes. Using the dependence of f_1 on C_2 as derived from Λ, λ_1° plots and taking for λ_p its value in blank polyelectrolyte solutions, the fraction of bound Zn^{2+} can be calculated from the conductivity excess. In fig. 4 the resulting f_1 and f_2 values are shown for different C_2/C_1 ratios. The f_2 values were calculated using eq. 9 and are average values for the three alkali polyacrylate solutions. Error bars indicate the standard errors. As is inferred from fig. 4 f_2 is practically zero up to $C_2/C_1 = 0.45$, or in other words, the added Zn^{2+} is practically quantitatively bound over the major part of the titration. Similarly to the conductivity excess curves, the plot of f_1 vs. C_2/C_1 shows two linear parts and a more or less horizontal part. The first linear part is between $C_2/C_1 = 0$ and 0.25 (with statistics: $n = 6$, $R^2 = 0.999$, $F = 4000$) and the second between $C_2/C_1 = 0.30$ and 0.50 ($n = 5$, $R^2 = 0.998$, $F = 951$). The intersection of these two linear parts coincides, within 1%, with that of the corresponding part of the conductivity excess curve (fig. 3). At this stage of titration ξ_{net} $(= f_p\xi)$ is about 0.5. It should be noted that the monovalent ions are not completely free at this stage. In the region around $C_2/C_1 = 0.50$ the behavior of the polyelectrolyte system is less clear-cut. Here, the conductivity excess curves are not linear and changes in the dimensions of the polyion may occur, implying a change in λ_p. Consequently, beyond $C_2/C_1 \approx 0.50$ the fraction of free divalent ions cannot be calculated exactly. The two dashed parts of the f_2 curve represent two extremes: the upper curve is calculated neglecting any additional binding of Zn^{2+}, whereas the lower one is calculated assuming a constant λ_p. The first approach may overestimate f_2, while the second is an underestimation. However, it is obvious that both curves approach each other. Furthermore, for $C_2/C_1 > 0.55$, f_1 becomes independent of C_2/C_1. The observation suggests that binding of Zn^{2+} ceases beyond $C_2/C_1 = 0.55$. In this region ξ_{net}, like f_2, cannot be calculated exactly; estimations on the basis of limiting cases yield a value between 0.05 and 0.16. The general conclusion is

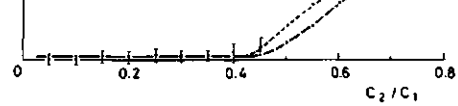

Fig. 4. Plots of f_1 and f_2 vs. the ratio C_2/C_1 for the alkali polyacrylate of fig. 3. Typical standard deviation in f_1 values is 0.01 and in f_2 values 0.04.

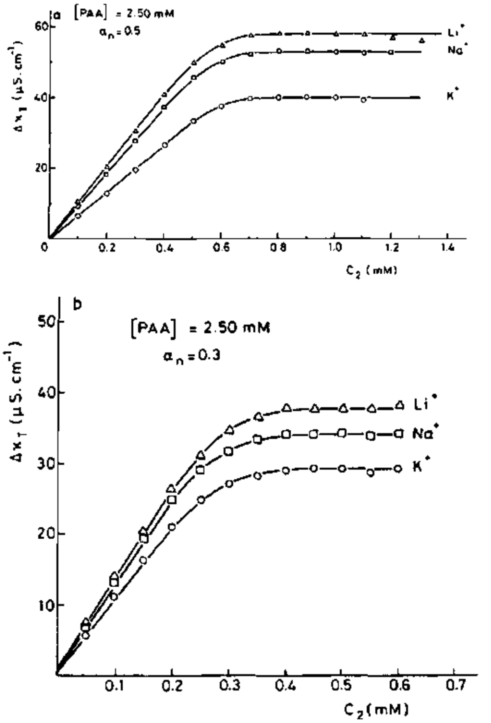

Fig. 5. Conductivity excess curves of alkali polyacrylate solutions as a function of the concentration of Zn(II). Standard deviations; see fig. 3.

that Zn^{2+} is completely bound at charge densities below 0.5.

In fig. 5 conductivity excess curves are shown for $\alpha_n = 0.3$ and $\alpha_n = 0.5$. As compared to the corresponding curves obtained for $\alpha_n = 0.8$ the kinks in the rising part are absent. In the curved parts of the plots, calculation of f_2 – using the value for λ_p obtained by conductance measurements in blank polyelectrolyte solutions – led to inconsistent results. This suggests that changes in the dimensions of the polyion, affecting its molar conductivity, may occur in the curved regions. Without knowledge of λ_p in these regions, conductivity data cannot be interpreted quantitatively. Here additional experiments are necessary to obtain λ_p. Generally, it appears that only the linear parts of the conductivity excess curves may be analyzed successfully.

In fig. 6, θ_1 and θ_2 are plotted vs. the ratio C_2/C_1 for $\alpha_n = 0.3$, 0.5 and 0.8. Taking into account an experimental error of typically 0.04, the bound fraction of Zn(II) does not vary significantly with the degree of neutralization. Under the present conditions, all added Zn^{2+} is quantitatively bound at any degree of neutralization of the polyion.

4.4. *Competition between monovalent and divalent counterions*

According to Poisson-Boltzmann calculations a 1 : 1 exchange of bound monovalent counterions against added divalent counterions should be expected for titration of a polyelectrolyte solution with a divalent salt [22]. The same was predicted by Miyamoto and Imai [23], who gave an analysis of the competition between mono- and divalent counterions based on the Poisson and Fokker-Planck equations. Condensation theory predicts that two bound monovalent counterions will be exchanged for one added divalent counterion [13,24]. In the first part of the titration, i.e., $0 < C_2/C_1 \leq 0.25$, the exchange ratio $r = -d\theta_1/d(1-f_2)C_2$ was 1.13 ± 0.04 for $\alpha_n = 0.8$, which is not too far from a 1 : 1 exchange. In the second part of the titration, i.e., $0.30 \leq C_2/C_1 \leq 0.45$, fewer bound monovalent counterions are displaced per bound divalent ion. Here, $r = 0.64 \pm 0.05$. Possibly in the first part of the titration counterion exchange takes place in the immediate vicinity of the polyion, which is the case that Guéron and Weisbuch [22,25] dealt with, whereas in the second part exchange occurs in a region where the monovalent counterions are not too close to the polyion, but are nevertheless restricted in mobility. The existence of such a region of restricted mobility, together with one close to the polyion and another in which the counterions are not influenced by the electric field of the polyion has been advocated by Magdélenat et al. [20].

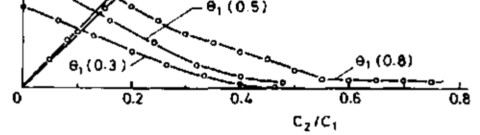

Fig. 6. Plots of θ_1 and θ_2 vs. the ratio C_2/C_1 for several degrees of neutralization. Typical standard deviation in θ_1 values is 0.01 and in θ_2 values 0.04.

For $\alpha_n = 0.5$ a 1 : 1 exchange for bound monovalent counterions and added divalent counterions is found over the entire accessible range. The same results were obtained for Ca^{2+}/Na^+ competition in aqueous solutions of a maleic acid copolymer studied by potentiometry [26]. At $\alpha_n = 0.3$, how-

Table 1

Bound fractions and conductivity data of alkali polyacrylate solutions at different degrees of neutralization

[PAA] = 2.50 mM in the presence of $Zn(NO_3)_2$.

	α_n		
	0.3	0.5	0.8
$1-f_{1,0}$	0.305 ± 0.005	0.429 ± 0.003	0.531 ± 0.005
$1-f_2$	1.09 ± 0.04	1.09 ± 0.05	0.99 ± 0.02
r	0.74 ± 0.05	1.01 ± 0.07	1.13 ± 0.04 [a]
			0.64 ± 0.04 [a]
λ_p (S cm^2 mol^{-1})	45.6 ± 0.8	39.8 ± 0.7	31.1 ± 0.9

[a] See text.

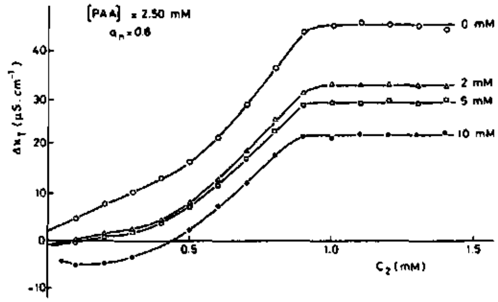

Fig. 7. Conductivity excess curves of potassium polyacrylate solutions for the indicated potassium nitrate concentrations, as a function of the concentration of Zn(II). In the worst case (10 mM KNO_3) the standard deviation of $\Delta\kappa_T$ values was typically about 1 μS cm^{-1}.

ever, more Zn^{2+} needs to be bound to release the same amount of bound monovalent ions. The results of the analysis given so far are summarized in table 1.

4.5. The case with an added 1 : 1 salt

In fig. 7 the conductivity excess curves for potassium polyacrylate at several KNO_3 concentrations are shown. Up to 5 mM KNO_3 the shapes of the conductivity excess curves are similar. From about 10 mM, significant deviations from this shape are observed. At this KNO_3 concentration the conductivity excess curves were not easy to interpret and evaluation as outlined in section 2 led to inconsistent results. Nevertheless, it appears that in the beginning of the titration the added Zn^{2+} is not completely bound in contrast to the case for a low concentration of 1 : 1 electrolyte. Perhaps, at the high salt concentrations binding of monovalent counterions is favored by their excess. This behavior was also reported by Magdelénat et al. [27] and Ishikawa [28].

Table 2

Bound fractions and conductivity data of alkali polyacrylate solutions at different concentrations of added alkali nitrate $[NO_3^-]_a$

$[PAA] = 2.50$ *mM and* $\alpha_n = 0.8$ *in the presence of* $Zn(NO_3)_2$.

	$[NO_3^-]_a$ (mM)		
	0	2	5
$\theta_{1,0}$	0.531 ± 0.005	0.510 ± 0.006	0.504 ± 0.008
$1-f_2$	0.99 ± 0.02	0.94 ± 0.06	0.95 ± 0.05
r	1.13 ± 0.04	1.21 ± 0.08	1.19 ± 0.09
	0.64 ± 0.04	0.67 ± 0.05	0.63 ± 0.08
λ_p(S cm^2 mol^{-1})	31.1 ± 0.9	17 ± 2	11 ± 2

In table 2 results for alkali polyacrylates with a degree of neutralization of 0.8 at several salt concentrations below 10 mM are summarized. It can be seen that the composition of the counter charge around the polyion is not influenced by the alkali nitrate concentration provided it remains below 5 mM. The internal consistency of the results for $(1-\theta_{1,0})$ is confirmed by the very good agreement with the results obtained from radioactive diffusion measurements by Ander et al. [29]. These findings further support the assumed additivity rule for the conductivity of polyelectrolyte solutions. The insensitivity of the fraction of bound divalent counterions for a limited excess of added 1 : 1 salt was also found by Magdelénat for Sr^{2+} in a solution of Na chondroitin sulfate and NaCl using radioactive tracer diffusion measurements [27].

For the case of an excess of 1 : 1 salt, the Poisson-Boltzmann equation was numerically integrated. The exchange ratio r was found to be 0.8 for a cylindrical charge distribution with a charge density corresponding to PAA with $\alpha_n = 0.8$. For low charge densities the calculated r decreases to about 0.7. These preliminary computations are in qualitative agreement with the observed tendency of r to decrease with decreasing charge density (see table 2). It is curious in this respect that, in the conductometric part of their study on the binding of Zn^{2+} to polymethacrylate anions in 10 mM KNO_3, Kolawole and Olayemi [6] paid no attention at all to the release of bound monovalent counterions upon addition of divalent counterions.

5. Conclusion

Conductometry is a valuable tool in the analysis of ion distributions in metal/polyelectrolyte systems. For the zinc/polyacrylate systems in

$LiNO_3$, $NaNO_3$ and KNO_3 solutions, the relationship between Λ and λ_1^0 as well as that between the conductivity excess and C_2 was linear. This allows the computation of the bound fractions of both the monovalent and divalent counterions. Up to a certain concentration level, the composition of the counterionic atmosphere around the polyion was insensitive to the added alkali nitrate. The M^+/M^{2+} exchange ratio r shows a discrete behavior and it was found to be dependent on both the degree of neutralization of poly(acrylic acid) and the amount of bound divalent counterions. For high α_n, r is close to unity over a particular range of M^+/M^{2+} ratios.

Acknowledgement

The authors are obliged to W.F. Threels for carrying out part of the experiments.

References

1 H. Eisenberg, J. Polym. Sci. (1958) 47.
2 J.C.T. Kwak and R.C. Hayes, J. Phys. Chem. 79 (1975) 265.
3 W.P.J.T. van der Drift, Thesis, State University, Utrecht, The Netherlands (1975).
4 R.F.M.J. Cleven, Thesis, Agricultural University, Wageningen, The Netherlands (1984).
5 J. Szymczak, P. Holyk and P. Ander, J. Phys. Chem. 79 (1975) 269.
6 E.G. Kolawole and J.Y. Olayemi, Macromolecules, 14 (1981) 1050.
7 D. Bratko, N. Celija, D. Dolar, J. Span, L. Trnkova and V. Vlachy, Macromol. Chem. Rapid Commun. 4 (1983) 783.
8 G.S. Manning, Biopolymers 9 (1970) 1543.
9 A. Schmitt and R. Varoqui, J. Chem. Soc. Faraday Trans. 2 69 (1973) 1087.
10 J.R. Huizenga, P.F. Grieger and F.T. Walk, J. Am. Chem. Soc. 72 (1950) 2636.
11 G.S. Manning, Q. Rev. Biophys. 11 (1978) 179.
12 M. Kowblansky and P. Zema, Macromolecules 14 (1981) 166, 1448.
13 P. Ander and M. Kardan, Macromolecules 17 (1984) 2431.
14 H. Vink, J. Chem. Soc. Faraday Trans. 1 77 (1981) 2439.
15 I. Noda, M. Nagasawa and M. Ota, J. Am. Chem. Soc. 86 (1964) 5075.
16 T. Kitano, A. Taguchi, I. Noda and M. Nagasawa, Macromolecules 13 (1980) 57.
17 G.S. Manning, J. Phys. Chem. 79 (1975) 262.
18 N. Imai and K. Iwasa, Isr. J. Chem. 11 (1973) 223.
19 B.E. Conway, Electrochemical data (Elsevier, Amsterdam, 1952).
20 H. Magdelénat, P. Turq, P. Tivant, M. Chemla, R. Menez and M. Drifford, Biopolymers 18 (1979) 187.
21 J.F. Thibault and M. Rinaudo, Biopolymers 24 (1985) 2131.
22 G. Weisbuch and M. Guéron, J. Phys. Chem. 85 (1981) 517.
23 S. Miyamoto and N. Imai, Biophys. Chem. 11 (1980) 345.
24 G.S. Manning, in: Polyelectrolytes, ed. E. Sélégny (Reidel, Dordrecht, The Netherlands, 1974) p. 9.
25 M. Guéron and G. Weisbuch, Biopolymers 19 (1980) 353.
26 T. Shimizu, A. Minakata and N. Imai, Biophys. Chem. 14 (1981) 333.
27 H. Magdelénat, P. Turq and M. Chemla, Biopolymers 13 (1974) 1535.
28 M. Ishikawa, Macromolecules 12 (1979) 502.
29 P. Ander and M. Kardan, Macromolecules 17 (1984) 2436.

SUMMARY

The present study is concerned with the electroanalytical chemistry of complexes of metals with large ligands. The main purpose was to develop quantitative descriptions of the voltammetric current-potential relation of metal complex systems with different diffusion coefficients of the species involved and of the conductometric response of metal/polyelectrolyte systems at various metal-to-ligand ratios. A further goal was to illustrate the theoretical treatments with some experiments on model systems.

In chapter 1 the general background of this study is discussed. After a brief review of some environmental aspects of heavy metals, the importance of reliable analytical techniques for their speciation is advanced. The particular potentialities of electroanalytical techniques in this field are outlined.

In chapter 2 a rigorous theoretical treatment is given of the voltammetric limiting current for metal complex systems in which the diffusion coefficents of the species involved are different. The equation for the limiting current is formulated in the Laplace domain and is rigorous with respect to the values of the association and dissociation rate constants as well as to the ratio of the diffusion coefficients of the species. It is valid for an excess of ligand and a stationary planar electrode. In some limiting cases analytical expressions in the time domain have been obtained. In the degenerate case of equal diffusion coefficients the limiting current can be described by a series expansion of confluent hypergeometric functions. Another limiting case is the situation where the diffusion coefficient of the ligand is infinitely small. Here, the use of a perturbation technique leads to a satisfactory approximation in the form of a series of confluent hypergeometric functions, for the case where the diffusion coefficient of the ligand is at least one order of magnitude smaller than that of the uncomplexed metal ion. Where analytical inversion of the Laplace transformed limiting current expression fails, transients are obtained by a numerical procedure. The results are identical with what may be obtained from the time-consuming fully numerical solution of the differential equations using the explicit finite difference algorithm.

In chapter 3 the behaviour of the limiting current is investigated as a function of the electrolysis time, the ratio of the diffusion coefficients of the species and the association/dissociation rate constants. New qualifications to specify the voltammetric behaviour of metal complex systems are

introduced. Depending on the mean life-times of the species, the system can be static, semi-dynamic and dynamic. When the mean life-times are large compared to the electrolysis time, the system is static and the limiting current is proportional to the concentration of uncomplexed metal. In the opposite case where the life-times are small compared to the electrolysis time, the system is dynamic. A dynamic system can be further subdivided in labile and non-labile. The lability concept unambiguously follows from considering the limiting cases in the theory. A new lability criterion is formulated, which is, compared to earlier tentative formulations, generalized to the metal complex system as a whole. In the non-labile regime the limiting current is found to follow exactly the classical reaction layer model, provided there is a large excess of complex over free metal. In order to facilitate practical use of the various results, some Cottrell plots and working curves are given.

In chapter 4 a rigorous treatment of the complete current-potential relation of the metal complex systems from the previous chapters is given. The general relation is again formulated in the Laplace domain. Besides its limitation to reversible electrode processes, it has the same range of validity as the limiting current equation of chapter 2. The half-wave potential is obtained numerically from the general current-potential relation and its dependence on the electrolysis time, the ratio of the diffusion coefficients of the species and the association/dissociation rate constants is discussed. In the case of equal diffusion coefficients of the species, the current-potential relation can be analytically transformed from the Laplace- to the time domain. The result is given as a series expansion of confluent hypergeometric functions. In the dynamic regime the current-potential relation is described by an experfc type of function. An analytical expression for the half-wave potential is then obtained. In the case of a labile system and a large excess of complex this expression reduces to the well-known DeFord-Hume equation.

In chapter 5 experimental data from earlier work on the voltammetry of heavy metal/polyelectrolyte systems are reconsidered. A procedure for solving a voltammetric speciation problem for a given set of values of the electrolysis time and the ratio of the diffusion coefficients is presented. Under the given experimental conditions the Zn/PMA system was found to be labile. Here the speciation is straightforwardly performed using the mean diffusion coefficient concept. The Cd/PMA data are substantially affected by induced adsorption of the metal ion. Until this is eliminated, interpretation is not possible. The Pb/PAA system seems to be dynamic and not labile. Here, the speciation is involved and performed by fitting the experimental data to the rigorous equations of the chapters 2 and 4 and as a result the order of magnitude of both the stability constant and the dissociation rate constant are obtained. Anticipating future presentations the correctness of the stability constant evaluated under the assumption of an excess of ligand, is estimated.

In chapter 6 a procedure is described for the analysis of the conductivity of solutions of polyions in which both mono- and divalent counterions are present. The method is based on analysis of the relation between the overall conductivity of the system and the conductivity of the monovalent cations and assumes that the latter are electrostatically bound. The system is described in terms of the two state approach, implying that the counterions are considered to be either in some kind of bound state or are completely free. The potentialities of the proposed method are explored by studying solutions of alkali polyacrylates with and without added zinc nitrate at several alkali nitrate concentrations The results give a picture of the composition of the counterionic atmosphere around the polyion. Up to a certain Zn/polyacrylate ratio, the zinc ions were found to be bound quantitatively by the polyion. The composition of the counterionc atmosphere was largely independent of the alkali nitrate concentration if the latter was not in too large excess with respect to both the zinc ions and the charged monomers.

ELECTROCHEMISCHE ANALYSE VAN ZWAAR METAAL COMPLEXEN

SAMENVATTING

Al eeuwen lang maakt de mens gebruik van metalen. In prehistorische tijden was hij reeds in staat bronzen en ijzeren werktuigen te vervaardigen. Geleidelijk aan vonden ook zouten van metalen hun toepassing. Zo werd enkele honderden jaren geleden kopersulfaat toegepast als algenverdelger. Na de industriële revolutie bleef de productiviteit stijgen. Tegelijk hiermee stegen ook de concentraties (zware) metalen in ons milieu. Tegenwoordig zijn metalen niet meer weg te denken. Er is een enorme verscheidenheid aan legeringen ontwikkeld, ieder met hun specifieke eigenschappen en toepassingen. Behalve in duidelijk herkenbare vormen, komen metalen en i.h.b. zware metalen (dat zijn b.v. cadmium, chroom, koper, lood, ijzer en zink) ook verstopt in allerlei alledaagse produkten voor. Zo zijn bepaalde soorten verf- en kleurstoffen gebaseerd op lood- of cadmiumverbindingen. In vele soorten batterijen bevinden zich zware metalen : lood in autoaccu's, cadmium en nikkel in oplaadbare batterijen, zink in gewone wegwerpbatterijen en kwik in de 'knoopcellen' voor b.v. digitale horloges. Zware metalen komen in het milieu o.a. via : de uitstoot van smeltovens en voor velen heel wat dichterbij huis, uitlaatgassen van auto's met benzinemotoren. Wat betreft het laatste, aan benzine wordt een loodverbinding, terta-ethyllood, toegevoegd om de verbranding te verbeteren.

Hoewel de giftigheid van zware metalen reeds lang bekend is, heeft men zich tot halverwege onze eeuw nauwelijks zorgen gemaakt over het gebruik van deze stoffen en zeker niet over de verspreiding daarvan in het milieu. In het begin van de 70'er jaren, toen er in Japan ongeveer 50 mensen overleden en 150 blijvend letsel opliepen na het eten van met kwik vergiftigde vis, drong de problematiek rond zware metalen in het milieu pas goed door.

De giftigheid van zware metalen wordt hoofdzakelijk bepaald door : (i) de aard van het zwaar metaal, zo is b.v. kwik giftiger dan zink en (ii) door de chemische verschijningsvorm, zo is koper gebonden aan slib veel minder giftig dan vrij koper. De giftigheid van zware metalen wordt veroorzaakt doordat zij gemakkelijk met eiwitten binden (complexeren). Zware metalen kunnen door binding met enzymen - stoffen die nodig zijn om biologisch belangrijke processen zoals het verteren van voedsel, de energie huishouding enz. gaande te houden - een ziekmakend effect hebben. Door complexering met DNA, de drager van erfelijke informatie, kunnen zware metalen kankerverwekkend zijn (carcinogeen effect) en (cel)groei processen vervormen (mutageen effect). Nu hebben zware metalen natuurlijk niet altijd en onmiddellijk dergelijke kwalijke gevolgen, veel hangt af van de dosis en tijdsbestek waarover men die binnen krijgt. Sommige zware metalen zoals chroom, koper, molybdeen, tin, ijzer en zink zijn essentieel voor dierlijk leven. Bij de mens kent men, behalve problemen met te grote hoeveelheden zware metalen, ziektebeelden voor een tekort aan ijzer (bloedarmoede), koper en zink.

Het zal nu wel duidelijk zijn dat er betrouwbare analyse technieken nodig zijn om zwaar metaal concentraties in milieu en medisch relevante monsters te kunnen bepalen. Dergelijke technieken, liefst gemakkelijk te automatiseren, moeten in het ideale geval niet alleen buitengewoon lage concentraties kunnen meten, maar ook nog onderscheid kunnen maken naar de chemische verschijningsvorm. (Is het aanwezige koper gebonden aan slib of is het helemaal vrij ?) Het specificeren van de verschillende chemische verschijningsvormen noemt men speciatie. Technieken die het geschetste probleem volledig aankunnen zijn er nog niet. Een van de meest veelbelovende in dit verband is de voltammetrie, een electroanalytische methodiek waarbij de concentratie van een stof wordt bepaald door deze aan een geschikte electrode een reactie te laten ondergaan. De hierbij optredende electrische stroom is een maat voor de concentratie van die stof. Nu komen in de natuur allerlei stoffen voor waarmee zware metalen complexeren ('binden'). Veel van die stoffen bestaan uit deeltjes die veel groter zijn dan het metaal deeltje zelf. Een complex ('verbinding') van beide zal daarom in een stilstaande vloeistof veel langzamer bewegen. In de voltammetrie wordt het signaal bepaald door de toevoer van materiaal, hier : het metaal deeltje en het complex, naar de electrode en daarom is de grootte van het complex van groot belang voor het signaal. Aan dit aspect is in de electrochemische literatuur nog maar heel weinig aandacht besteed.

Het voornaamste deel van dit proefschrift handelt over de theorie van voltammetrie van metaal complex systemen waarin de grootte van het complex en het metaal deeltje verschillend zijn. (Hoofdstuk 2, 3 en 4). Er zijn in een speciale wiskundige ruimte vergelijkingen voor de stroom ('het signaal') en voor het verband tussen de gemeten stroom en de aangelegde spanning afgeleid. Aangezien deze wiskundige ruimte geen directe natuurkundige betekenis heeft, men kan er geen metingen in verrichten, moeten de vergelijkingen naar een wel toegankelijke ruimte, onze natuurkundige tijd-ruimte worden overgebracht. Dit is analytisch (d.w.z. in wiskundige formule vorm) alleen in enkele meer en minder eenvoudige randgevallen mogelijk. Voor het overige is gebruik gemaakt van een numerieke methode, d.w.z. de oplossing wordt in de vorm van getallenreeksen verkregen die m.b.v. een computer zijn berekend. Op basis van theoretische beschouwingen zijn een aantal nieuwe kwalificaties geïntroduceerd om het gedrag van metaal complex systemen te beschrijven.

Met de theorie in de hand zijn een aantal experimenten uit vroeger werk opnieuw bekeken (hoofdstuk 5). Er is gekozen voor experimenten aan modelsystemen, met als complexvormers, polyzuren, die kwa eigenschappen sterk lijken op in de natuur voorkomende complexvormers (fulvo- en humuszuren), maar waarvan de chemische structuur exact bekend is. De experimenten zijn uitgevoerd met cadmium, lood en zink. Afgezien van de meetresultaten voor cadmium, waar adsorptie als extra complicatie optreedt, lijkt de nieuw ontwikkelde theorie de voltammetrische speciatie een stap vooruit te brengen.

Naast voltammetrie wordt bij de bestudering van complexen vaak nog conductometrie gebruikt. Hierbij wordt de electrische geleiding van de oplossing gemeten. Deze techniek is vanwege de bescheiden detectiegrens niet zo zeer geschikt voor de analyse van milieu monsters maar kan gegevens opleveren die inzicht verschaffen in de mate waarin metalen complexeren. Uitgaande van de bestaande theorie, is een analyse procedure ontwikkeld en getest op een modelsysteem t.w. zink en een synthetische complexvormer (polyacrylzuur). De resultaten geven een kwantitatief beeld van de wisselwerking tussen het zwaar metaal en de complexvormer.

CURRICULUM VITAE

Op 26 juni 1959 ben ik geboren te Nieuwkoop. In 1977 behaalde ik het diploma Atheneum B aan het Hermann Wesselink College te Amstelveen. In hetzelfde jaar werd ook begonnen met de studie Scheikunde aan de Vrije Universiteit te Amsterdam. Het doctoraal examen werd met lof behaald in 1983. De doctoraal studie omvatte de vakken Analytische Chemie (uitgebreid hoofdvak) en Farmacochemie (bijvak).

Van september 1983 tot december 1987 was ik verbonden aan de vakgroep Fysische en Kolloidchemie van de Landbouwuniversiteit. In deze periode vond het onderzoek plaats dat tot dit proefschrift leidde.

DANKWOORD

Dit proefschrift is voortgekomen uit een onderzoek dat plaats gevonden heeft tijdens een periode van vier jaar. Een ieder die hieraan een bijdrage heeft geleverd ben ik veel dank verschuldigd. Enkele mensen wil ik persoonlijk noemen.

Aan mijn co-promotor, Herman van Leeuwen, dank ik een belangrijk deel van de uiteindelijke inhoud van dit proefschrift. Zijn briljant vakmanschap is voor mij de beste leerschool geweest, die ik mij wat betreft "het vak" kon wensen. Herman, bedankt !

Hans Lyklema, mijn promotor dank ik voor de grote mate van vrijheid die hij mij bij de uitvoering van het onderzoek heeft gelaten. Zijn kritische en bijzonder grondige commentaren op het manuscript waren vaak aanleiding tot bezinning mijnerzijds.

Willem Threels dank ik voor de kalme en volhardende wijze waarop hij de conductometrische titraties heeft uitgevoerd.

Gerrit Buurman heeft op voortreffelijke wijze zorg gedragen voor het produceren van de figuren.

Henny van Beek, Rob Vullings en Ronald Wegh waren zeer behulpzaam bij de mechanica en de electronica van de experimenten. Vooral de soepele uitvoering van de "kleine klusjes tussendoor", maakten dat de voortgang van de experimenten niet al te zeer stagneerde.

Ben Spee en Willem van Maanen bleken meesters in het "organiseren" van allerlei onmisbare laboratoriumattributen en chemicaliën.

Bertha Versteeg heeft een flink deel van het manuscript op zorgvuldige wijze getypt. Ik ben mij er van bewust dat dit niet altijd een gemakkelijke klus is geweest.

Tenslotte dank ik Elsevier Science Publishers voor de vriendelijke toestemming voor het reproduceren van de hoofdstukken 2, 3, 4 en 6.