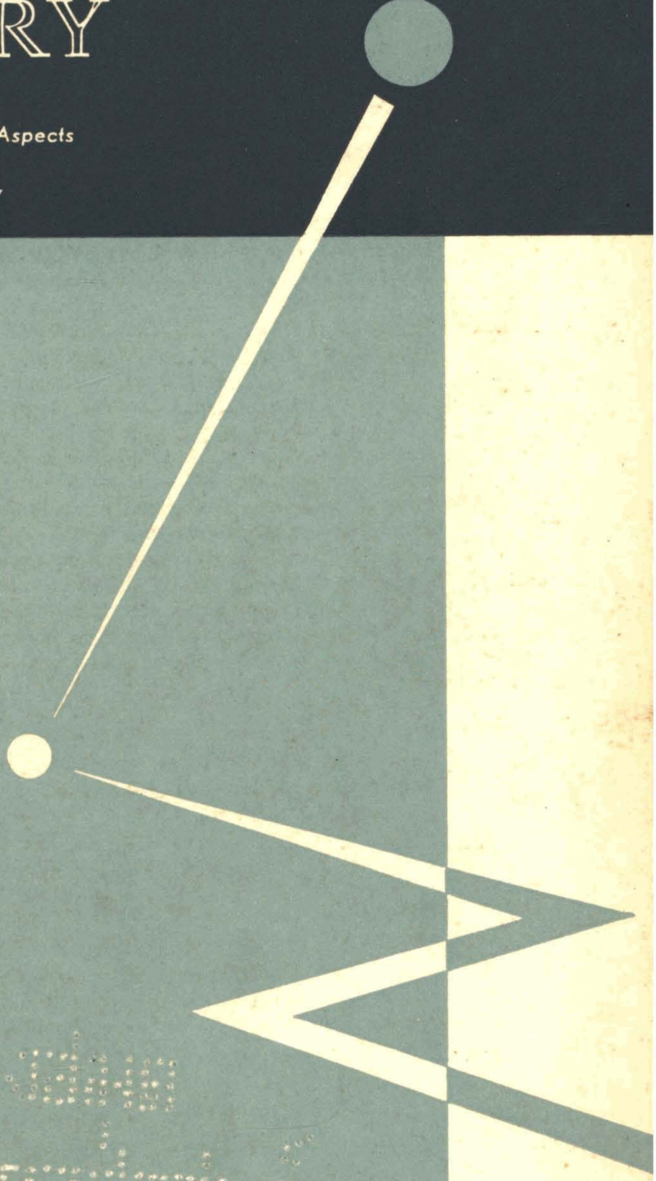
VOL. 8 NO. 1 JULY 1964
PUBLISHED MONTHLY

Journal of ELECTROANALYTICAL CHEMISTRY

International Journal Dealing with all Aspects
of Electroanalytical Chemistry,
Including Fundamental Electrochemistry



ELSEVIER

GENERAL INFORMATION

See also Suggestions and Instructions to Authors which will be sent free, on request to the Publishers.

Types of contributions

- (a) Original research work not previously published in other periodicals.
- (b) Reviews on recent developments in various fields.
- (c) Short communications.
- (d) Bibliographical notes and book reviews.

Languages

Papers will be published in English, French or German.

Submission of papers

Papers should be sent to one of the following Editors:

Professor J. O'M. Bockris, John Harrison Laboratory of Chemistry,
University of Pennsylvania, Philadelphia 4, Pa., U.S.A.
Dr. R. Parsons, Department of Chemistry,
The University, Bristol 8, England.
Professor C. N. Reilley, Department of Chemistry,
University of North Carolina, Chapel Hill, N.C., U.S.A.

Authors should preferably submit two copies in double-spaced typing on pages of uniform size. Legends for figures should be typed on a separate page. The figures should be in a form suitable for reproduction, drawn in Indian ink on drawing paper or tracing paper, with lettering etc. in thin pencil. The sheets of drawing or tracing paper should preferably be of the same dimensions as those on which the article is typed. Photographs should be submitted as clear black and white prints on glossy paper.

All references should be given at the end of the paper. They should be numbered and the numbers should appear in the text at the appropriate places.

A summary of 50 to 200 words should be included.

Reprints

Twenty-five reprints will be supplied free of charge. Additional reprints can be ordered at quoted prices. They must be ordered on order forms which are sent together with the proofs.

Publication

The *Journal of Electroanalytical Chemistry* appears monthly and has six issues per volume and two volumes per year, each of approx. 500 pages.

Subscription price (post free): £ 10.15.0 or $ 30.00 or Dfl. 108.00 per year; £ 5.7.6 or $ 15.00 or Dfl. 54.00 per volume.

Additional cost for copies by air mail available on request.

For advertising rates apply to the publishers.

Subscriptions

Subscriptions should be sent to:

ELSEVIER PUBLISHING COMPANY, P.O. Box 211, Amsterdam, The Netherlands.

SUMMARIES OF PAPERS PUBLISHED IN JOURNAL OF ELECTROANALYTICAL CHEMISTRY

Vol. 8, No. 1, July 1964

THE CONTRIBUTION OF ELECTROSTATIC COUPLING TO ELECTRICAL MIGRATION IN CHRONOPOTENTIOMETRY

The nature and effect of electrostatic coupling in chronopotentiometry are considered. General flow equations are presented. The Morris–Lingane equation describing the variation of transition time with supporting electrolyte concentration is shown to follow from a simplified form of the general equations. The discrepancies between the Morris–Lingane treatment and experiment are explained.

M. D. MORRIS,

J. Electroanal. Chem., 8 (1964) 1–4.

THE INFLUENCE OF HYDROLYSIS ON THE DEPOSITION AND CO-DEPOSITION OF IRON-GROUP METALS (Fe, Co, Ni) AT THE DROPPING MERCURY ELECTRODE

The deposition and co-deposition of iron(II), cobalt(II) and nickel(II) ions were studied polarographically in weakly acid (pH 3–5.5) solutions. Variation of pH in this region does not affect the waves. By adding oxygen to the solution, high pH values were generated at the electrode surface ($O_2 + 2\ H_2O + 4\ e \rightarrow 4\ OH^-$) leading to hydrolysis of the discharging metal ions. Hydrolysis not only reduces the concentration of the discharging species due to $Me^{2+} + 2\ OH^- \rightarrow Me(OH)_2\downarrow$ but also leads to adsorption of hydroxides at the interface. Chronopotentiometric measurements showed that about $3 \cdot 10^{-10}$ moles/cm^2 $Fe(OH)_2$ are adsorbed at the electrode. Hydrolysis changes the rate of single metal discharge only slightly, but has a strong effect on the co-deposition of metals. The discharge of one metal can be suppressed by the presence of a second iron-group metal. Ferrous ions cause the strongest suppression followed by cobaltous ions. The same sequence ($Fe^{2+} > Co^{2+} > Ni^{2+}$) is found in the suppression of Tl^+ discharge. This sequence is interpreted on the basis of adsorption measurements.

H. DAHMS,

J. Electroanal. Chem., 8 (1964) 5–12.

DIRECT MEASUREMENT OF THE DIFFUSION COEFFICIENTS OF IONS IN AQUEOUS SOLUTION IN PRESENCE OF A SUPPORTING ELECTROLYTE

Philpot-Svenson's oblique slit method for the measurement of the diffusion coefficients of ions or molecules in solutions containing an excess of supporting electrolyte has been adapted. The tests were carried out for hydroquinone in 0.5 *M* sulfuric acid.

The scatter of the measurements varies from 1.2 to 1.8% between 2.8 and 25°.

The system studied follows the Stokes-Einstein relation.

A. M. BATICLE,

J. Electroanal. Chem., 8 (1964) 13–19.

EFFECTS OF ANIONS AND CATIONS ON OXYGEN REDUCTION AND OXYGEN EVOLUTION REACTIONS ON PLATINUM ELECTRODES

The effects of the addition 10^{-4}–10^{-1} M of various anions and cations to 1 N H_2SO_4 or 1 M NaOH solutions on oxygen-reduction at pre-anodized and pre-cathodized platinum electrodes were examined by measuring coulombic efficiency for formation of hydrogen peroxide (calculated on the basis of $O_2 + H_2O + 2\,e \rightarrow OOH^- + OH^-$) and also by current–potential curves. In 1 M NaOH, oxygen was reduced to hydrogen peroxide with an efficiency of almost 100% at the pre-anodized electrode. However, in the presence of Ba^{2+}, Sr^{2+}, and Ca^{2+} in 1 M NaOH, the efficiency decreased to 10–15% with increasing concentration of the ions. In 1 N H_2SO_4, oxygen was reduced mainly to water and the coulombic efficiency for hydrogen peroxide formation was only 10–20%, but in the presence of Cl^- and Br^- ions this efficiency increased to 50–60%. Current–potential curves indicated that overpotential of the oxygen reduction at the platinum electrodes increased in the presence of Ba^{2+}, Sr^{2+}, and Ca^{2+} ions in 1 M NaOH, and in the presence of Cl^- and Br^- ions in 1 N H_2SO_4. Catalytic activity of the platinum electrodes for hydrogen peroxide decomposition in 1 M NaOH and 1 N H_2SO_4 with and without the addition of the anions and cations was also measured.

These results are discussed on the basis of ion-exchange adsorption of cations and anions on the oxide-covered platinum electrodes. It is concluded that the oxygen reduction on platinum is not one process, but at least two processes including $O_2 + H_2O + 2\,e \rightarrow OOH^- + OH^-$ in alkaline solution and $O_2 + 2\,H^+ + 2\,e \rightarrow H_2O_2$ in acid solution, and the proportion of hydrogen peroxide formation depends on the surface condition of the electrode, such as presence of oxide film and/or adsorption of anions and cations.

Oxide films and/or adsorbed oxygen which exist on the platinum electrodes were summarized and a voltammetric study of a special oxide film formed on an excessively anodized platinum electrode was described. Overpotential of oxygen evolution on other metals and graphite as well as on Pt in 1 M NaOH increased by $15 \sim 90$ mV when Ba^{2+}, Sr^{2+}, or Ca^{2+} ions were added to the electrolyte.

A. Kozawa,

J. Electroanal. Chem., 8 (1964) 20–39.

DERIVATIVE POLAROGRAPHIC TITRATION OF TERTIARY AMINES AND SALTS OF ORGANIC ACIDS IN ACETIC ACID IN THE PRESENCE OF ANTIMONY AND QUINHYDRONE ELECTRODES

Derivative polarographic titration of some tertiary amines and salts of organic acids with perchloric acid in a mixture of glacial acetic acid and acetic anhydride, with two antimony or quinhydrone electrodes is described. The advantages of the method over potentiometric titration are that a sharper end-point is obtained and the use of a reference electrode and a salt bridge is avoided. The rather long time required for the titration of certain systems is a disadvantage. Quinhydrone electrodes give sharper titration end-points than antimony electrodes, but titrations with the latter can be accomplished more rapidly. The results obtained are in very good agreement with those obtained by potentiometric titration and afford excellent reproducibility.

V. Vajgand and T. Pastor,

J. Electroanal. Chem., 8 (1964) 40–48.

DETERMINATION OF TERTIARY AMINES AND SALTS OF ORGANIC ACIDS IN GLACIAL ACETIC ACID BY DEAD-STOP METHOD

In this work, compounds containing tertiary nitrogen and salts of organic acids were titrated with perchloric acid by a dead-stop method in a mixture of glacial acetic acid and acetic anhydride. With antimony electrodes the stationary state was quickly established, the current was stable and the end-point was indicated by a sharp minimum in the current. Titrations in the presence of quinhydrone electrodes required a longer time and at the titration end-point the current was sharply reduced to a value which remained constant on further titration.

The effect of various amounts of acetic anhydride on the sharpness of the end-point in the presence of antimony, and quinhydrone electrodes has also been studied.

V. VAJGAND AND T. PASTOR,

J. Electroanal. Chem., 8 (1964) 49–54.

ELECTROCHEMICAL BEHAVIOR OF COPPER IONS AND SILVER ION IN HYDRACRYLONITRILE AND SOME RELATED NITRILES

The electrochemical behavior of copper ions in hydracrylonitrile and related nitriles has been investigated. It is of interest to note that in hydracrylonitrile copper(II) ion is solvated by the nitrile group, whereas in 1 : 1 alcohol–nitrile mixtures, it is solvated by the hydroxyl group. This unusual situation appears to be due to the fact that hydracrylonitrile (dielectric constant, 65), 1 : 1 ethanol–acetonitrile mixture (dielectric constant, 32), and 1 : 1 1-butanol–propionitrile mixture are polar solvent systems and, therefore, favor the more polar solvated form of copper(II) ion. This, in hydracrylonitrile has the the solvent molecules oriented with the nitrile group attached to copper(II) ion and the hydroxyl group sticking out and forming a polar outer sheath and in 1 : 1 alcohol–nitrile mixture has alcohol rather than nitrile molecules in the co-ordination sphere. Nitrile-solvated copper(II) ion with an outer sheath consisting only of alkyl groups behaves like a non-polar solute.

In view of the absence of any solvent effect on the potentials of the copper couples in hydracrylonitrile, 3-butenenitrile, and in the alkoxypropionitriles, copper ions are most likely solvated by the *trans* conformer of these solvents. The effect of substituents in the 3-position in propionitrile *i.e.*, on the basicity of the nitrile group on the potentials of the copper couples, is consistent with the influence of the substituents on other functional groups in different compounds.

Except for the fact that silver(I) ion is reduced at potentials more positive than those at which copper(I) ion is reduced, the electrochemical reduction of silver(I) ion in hydracrylonitrile and related nitriles is similar to that of copper(I) ion.

F. FARHA, JR. AND R. T. IWAMOTO,

J. Electroanal. Chem., 8 (1964) 55–64.

REVIEW

GLOW-DISCHARGE ELECTROLYSIS

The methods and results of glow-discharge electrolysis have been reviewed and an attempt has been made to pick out the essential features of the process. It is interpreted as a form of electrolysis in which energy transfer as well as charge transfer is involved, and this serves to break up solvent molecules into reactive radicals which produce the chemical reactions observed. The energy is conveyed by gaseous ions accelerated in the electrical field near the liquid surface, and the process has much in common with radiolysis in which the individual particles are of low energy but the dose-rate is extremely high.

A. HICKLING AND M. D. INGRAM,

J. Electroanal. Chem., 8 (1964) 65–81.

A NOTE ON THE DESIGN AND HANDLING OF A STATIONARY DROP ELECTRODE

(Short Communication)

J. J. VOGEL,

J. Electroanal. Chem., 8 (1964) 82–84.

JOURNAL OF ELECTROANALYTICAL CHEMISTRY

VOL. 8 (1964)

JOURNAL
of
ELECTROANALYTICAL CHEMISTRY

INTERNATIONAL JOURNAL DEALING WITH ALL ASPECTS OF ELECTROANALYTICAL CHEMISTRY, INCLUDING FUNDAMENTAL ELECTROCHEMISTRY

VOL. 8 1964

ELSEVIER PUBLISHING COMPANY
AMSTERDAM

ELSEVIER PUBLISHING COMPANY, AMSTERDAM
Printed in The Netherlands by
NEDERLANDSE BOEKDRUK INRICHTING N.V., 'S-HERTOGENBOSCH

THE CONTRIBUTION OF ELECTROSTATIC COUPLING TO ELECTRICAL MIGRATION IN CHRONOPOTENTIOMETRY

MICHAEL D. MORRIS*

Department of Chemistry, Harvard University, Cambridge 38, Mass. (U.S.A.)

(Received March 1st, 1964)

In a recent communication MORRIS AND LINGANE[1] presented without proof an equation to describe the variation of the chronopotentiometric transition time with supporting electrolyte concentration (eqn. (31) of reference 1). This communication describes the origin of that equation and explains the discrepancies between it and experiment.

The discussion will be restricted to the case of the reduction of a metal ion in the presence of any amount of a supporting electrolyte, the anion of which is the same as the counter-ion to the reducible species. Examples of such a system are thallous sulfate–potassium sulfate and cupric sulfate–potassium sulfate, which have been studied by MORRIS AND LINGANE[1].

As the metal ion is reduced in such a system, a concentration gradient is set up and metal ion diffuses toward the electrode in response to that gradient. Metal ion also moves toward the cathode in response to the potential gradient. Simultaneously, an amount of anion exactly sufficient to maintain electrical neutrality moves in the other direction.

A concentration gradient of the non-reducible cation is also being built up. The magnitude of this concentration gradient will depend upon the relative concentrations of the two electrolytes present and upon the difference in mobilities of the three ions in solution. This gradient always acts in such a way as to lessen the effect of electrical migration.

In the formal derivation of the flow equations, the reducible cation is identified by the subscript, 1, the cation of the supporting electrolyte by the subscript, 2, and the common anion by the subscript, 3. The notation is consistent with that of reference 1 exept that the current density is here designated by i_0.

Flow equations of the form of eqn. (1) can be written for each of the three ionic species present

$$f_i = D_i \left[\frac{\partial C_i}{\partial x} + \frac{z_i C_i F}{RT}\frac{\partial \phi}{\partial x}\right] \quad i = 1, 2, 3 \tag{1}$$

---

* Present address: Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania, U.S.A.

For three ionic species the electro-neutrality relationship assumes the form

$$z_1C_1 + z_2C_2 = -z_3C_3 \tag{2}$$

The current density at any point in the solution is related to the weighted sum of the fluxes by

$$\frac{i_0}{F} = z_1f_1 + z_2f_2 + z_3f_3 \tag{3}$$

Equations (2) and (3) may be introduced into the system of eqns. (1) to eliminate the potential gradient terms and the terms in one of the concentrations. For convenience, terms in the anion concentration, C_3, are eliminated.

Performance of the necessary manipulations reduces the system of eqns. (1) to

$$f_1 = D_{1,1}\frac{\partial C_1}{\partial x} + D_{1,2}\frac{\partial C_2}{\partial x} + \frac{i_0}{z_1F}\frac{z_1^2C_1D_1}{\chi} \tag{4}$$

$$f_2 = D_{2,1}\frac{\partial C_1}{\partial x} + D_{2,2}\frac{\partial C_2}{\partial x} + \frac{i_0}{z_2F}\frac{z_2^2C_2D_2}{\chi} \tag{5}$$

where

$$D_{1,1} = D_1\left[1 - \frac{z_1z_1C_1(D_1 - D_3)}{\chi}\right] \tag{6}$$

$$D_{1,2} = -D_1\left[\frac{z_1z_2C_2(D_2 - D_3)}{\chi}\right] \tag{7}$$

$$D_{2,1} = -D_2\left[\frac{z_2z_1C_1(D_1 - D_3)}{\chi}\right] \tag{8}$$

$$D_{2,2} = D_2\left[1 - \frac{z_2z_2C_2(D_2 - D_3)}{\chi}\right] \tag{9}$$

and

$$\chi = z_1C_1(z_1D_1 - z_3D_3) + z_2C_2(z_2D_2 - z_3D_3) \tag{10}$$

$D_{1,1}$ and $D_{2,2}$ are the main diffusion coefficients. $D_{1,2}$ and $D_{2,1}$ are the cross-term diffusion coefficients.

To understand the significance of the three terms on the right-hand side of each of eqns. (4) and (5) it is useful to consider the case where $i_0 = 0$, that is, free diffusion in a system containing three ionic species.

If one electrolyte is allowed to diffuse through another, a concentration gradient of the initially homogenous electrolyte is built up and then decays as the solution approaches equilibrium. The experimental evidence has been reviewed by GOSTING[2]. The concentration gradient arises because of the unequal mobilities of the ions of the diffusing electrolyte. The faster ion tends to outrun the slower ions during diffusion. In order to maintain electro-neutrality, the ion of the common electrolyte of the same sign as the faster ion of the diffusing electrolyte moves in the opposite direction. The phenomenon is called electrostatic coupling.

By the same procedure used here to derive eqns. (4) and (5), GOSTING and co-workers[2] have derived equations to describe three-component ionic diffusion. GOSTING's equations do not contain terms in $z_i^2D_iC_i$ because they are derived from the premise that the net current in the solution is zero, not i_0. Otherwise they are identical with eqns. (4) and (5).

Comparison of eqns. (4) and (5) with the equations for free diffusion shows that the non-zero cross-term diffusion coefficients and the variable main diffusion coefficients appear here because of electrostatic coupling, the effect which the diffusion of one ion has on the concentration gradients of the others through the maintenance of electro-neutrality. The inconstancy of the D's in these equations results from the fact that the magnitude of the coupling depends upon the relative concentrations of the two electrolytes.

In the chronopotentiometric case, $D_{1,1}$ varies at the electrode surface from its value at the start of the electrolysis to D_1 at the transition time. $D_{1,2}$ varies from its initial value to zero at the electrode surface at the transition time, ($C_1(0,\tau) = 0$). These variations reflect the fact that electrostatic coupling becomes unimportant in the presence of excess supporting electrolyte and eqn. (4) reduces to Fick's first law.

The terms $z_1^2C_1D_1/\chi$ and $z_2^2C_2D_2\chi$ may be formally identified as the instantaneous transference numbers of the reducible and non-reducible cations. These transference numbers represent the fraction of the current carried by the reducible or non-reducible cation as a function of time and distance. The instantaneous transference number of the reducible cation approaches zero in the region of the electrode surface as the transition time is reached. The instantaneous transference number of the non-reducible cation approaches the value it has in a pure solution of the supporting electrolyte. In other words, the effect of electrical migration on the flux of the reducible cation diminishes during the course of a chronopotentiogram.

In order to render eqn. (4) tractable, MORRIS AND LINGANE[1] tacitly make the following assumptions: $D_{1,1}$ is held constant at some particular value; the instantaneous transference number, T_1, is held constant; the term $D_{1,2}\partial C_2/\partial x$ is set equal to zero.

MORRIS AND LINGANE choose the initial values of $D_{1,1}$ and T_1. With these assumptions eqn. (4) reduces to

$$f_1 = D_{1,1}\frac{\partial C_1}{\partial x} + \frac{i_0}{z_1F}T_1 \tag{11}$$

from which one can immediately write

$$\frac{\partial C_1}{\partial t} = D_{1,1}\frac{\partial^2 C_1}{\partial x^2} \tag{12}$$

The usual chronopotentiometric initial and boundary conditions obtain. Application of these conditions to eqn. (12) leads to the following expression

$$C_1(0,t) = C_1{}^0 - \frac{2(1 - T_1)i_0t^{\frac{1}{2}}}{n_1\pi^{\frac{1}{2}}D_{1,1}{}^{\frac{1}{2}}F} \tag{13}$$

or, at the transition time, τ

$$\frac{i_0\tau^{\frac{1}{2}}}{C^0} = \frac{n_1\pi^{\frac{1}{2}}D_{1,1}{}^{\frac{1}{2}}F}{2(1 - T_1)} \tag{14}$$

Equation (14) has been used by MORRIS AND LINGANE[1] to evaluate chronopotentiometric data for the reduction of thallous and cupric ions in the presence of various amounts of supporting electrolyte.

The estimate of the transition time provided by eqn. (14) will usually be greater than the experimental value. It is based on the assumption that there is no concentration gradient of the supporting electrolyte, and that the fraction of the current carried by the reducible cation remains at its initial value. But, as has been pointed out above, a concentration gradient of the supporting electrolyte must be set up if the ions have unequal diffusion coefficients and this gradient acts in such a way as to reduce the migration effect on the reducible cation. The migration effect is further over-estimated by the assumption that the transference number of the reducible cation remains constant. Since the forces causing transport of the reducible cation to the electrode surface are over-estimated in the derivation of eqn.(14), the time required to reduce the surface concentration of that ion to zero, the transition time, is over-estimated.

The degree of departure of eqn. (14) from experiment will depend upon the direction in which $D_{1,1}$ varies during the course of the chronopotentiogram. For the system thallous sulfate–potassium sulfate, $D_{1,1}$ increases during the electrolysis. The choice of the initial value, which is the smallest obtained by $D_{1,1}$, tends to compensate for the exaggeration of the migration effect in eqn. (14). MORRIS AND LINGANE[1] obtained good agreement between eqn. (14) and experiment for the reduction of thallous sulfate in the presence of various amounts of potassium sulfate. Since $D_{1,1}$ decreases throughout a chronopotentiometric reduction of copper sulfate in the presence of potassium sulfate, eqn. (14) should provide a less accurate description of this system, in accord with the findings of MORRIS AND LINGANE.

ACKNOWLEDGEMENTS

The author whishes to acknowledge the helpful discussions and advice of Professor JAMES J. LINGANE. The author is grateful to the National Institutes of Health, Division of General Medical Sciences for the grant of a Predoctoral Fellowship.

SUMMARY

The nature and effect of electrostatic coupling in chronopotentiometry are considered. General flow equations are presented. The Morris–Lingane equation describing the variation of transition time with supporting electrolyte concentration is shown to follow from a simplified form of the general equations. The discrepancies between the Morris–Lingane treatment and experiment are explained.

REFERENCES

1 M. D. MORRIS AND J. J. LINGANE, *J. Electroanal. Chem.*, 6 (1963) 300.
2 L. J. GOSTING, *Advances in Protein Chemistry*, Vol. XI, edited by M. L. ANSON, K. BAILEY AND J. T. EDSALL, Academic Press, Inc., New York, 1956, p. 429.

THE INFLUENCE OF HYDROLYSIS ON THE DEPOSITION AND CO-DEPOSITION OF IRON-GROUP METALS (Fe, Co, Ni) AT THE DROPPING MERCURY ELECTRODE

HARALD DAHMS

IBM Watson Research Center, Yorktown Heights, New York (U.S.A.)

(Received March 12th, 1964)

INTRODUCTION

The occurrence of hydrolysis due to local high pH values at the electrode is a common feature in the electrodeposition of the iron-group metals[1]. The presence of hydroxides has been observed at the electrode–solution interface[2] as well as in the electrodeposits obtained[3,4]. The participation of $MeOH^+$ in the rate-determining step of the discharge reaction has been postulated for all iron-group metals (Fe[5], Co[6], Ni[7]).

Although the existence and the importance of hydrolysed species in electrodeposition has been realized, their role in the electrodeposition of iron-group metals is by no means understood. Hypotheses range from the assumption of a blocking effect on the electrode surface and a decrease in the concentration of reactive species[4,8,9] to the postulation of their direct participation in the discharge[5-7]. Investigations on the effects of hydrolysis are complicated by the fact that hydrolysis is only one factor among several others[10,11] which affect the composition and the structure of the interface during deposition.

An investigation on the effects of hydrolysis at the dropping mercury electrode avoids several complications, mainly due to the fact that no simultaneous hydrogen discharge is taking place. A few observations have been made on the effect of pH on the polarographic behavior of Fe^{2+}, Ni^{2+} and Co^{2+}. IVANOV AND IOFA[12] observed a small shift of the iron-wave with changing pH. BRDIČKA[13] found a small "wave" in the discharge of cobaltous ions which he attributed to $CoOH^+$. On the other hand DANDOY AND GIERST[14] in their careful study of the discharge kinetics of Ni^{2+} came to the conclusion that the rate-determining step does not involve any hydrolysed species.

The mercury electrode enables the metal discharge reaction to be studied in both the presence and the absence of hydrolysis. Under ordinary polarographic conditions no local high pH values leading to hydrolysis will occur in the vicinity of the electrode. On the other hand, hydrolysis effects can be caused on the mercury electrode by hydroxide ions generated in reactions such as, *e.g.*, $O_2 + 2\ H_2O + 4\ e \rightarrow 4\ OH^-$, or $IO_3^- + 3\ H_2O + 6\ e \rightarrow I^- + 6\ OH^-$[15]. These features of the mercury electrode will be used here in order to establish the role of hydrolysis in deposition and co-deposition. So far, no attempts have been made to relate hydrolysis effects to phenomena occurring in the co-deposition of iron-group metals.

EXPERIMENTAL

The polarograms were obtained by conventional polarographic techniques except that instantaneous currents during drop life were measured in order to simplify interpretation of the results. The Sargent Model XV polarograph used was modified only by feeding the cell current into a fast recorder (Sargent Recorder MR, full scale deflection in 1 sec).

The cell, a standard H-type polarographic cell, was kept at 25 ± 1° by means of a water-jacket. The two compartments of the cell were separated only by a porous-glass disk. The inner resistance of the cell was below 10 Ω. A Hg/Hg_2SO_4, Na_2SO_4 (satd.) counter electrode was used, the potential of which was controlled against a saturated calomel electrode.

The adsorption of $Fe(OH)_2$ was measured by rapid galvanostatic charging (originated by BOWDEN[16]) utilizing the reaction $Fe(OH)_2 + OH^- - e \rightarrow Fe(OH)_3$. For these measurements, the flow-rate of mercury was adjusted so that a drop was formed approximately each 10 sec. The measurements were made at a drop life of 5 sec. At this time, the change-over from the constant potential to the constant current circuit was effected manually. For this purpose a special switch[17] was built with a switching time of less than 50 μsec. The constant current was provided by a 90-V battery source with a variable high resistance in series. The potential–time curves were recorded on an oscilloscope (Tektronix, Type 545A) and could be photographed by means of an attached camera (Tektronix C-12).

Solutions were prepared from reagent-grade chemicals and doubly-distilled water. High-purity nitrogen was used to remove other dissolved gases from the solution. Solutions containing dissolved oxygen were prepared from high-purity oxygen (Matheson), minimum purity 99.9%. The pH of the solution was measured immediately before and after an experiment in the cell by means of a glass electrode.

RESULTS

Figures 1–3 show the polarographic waves of the iron-group metals in N_2 (left-hand Figs.) and in solutions containing O_2. The flow-rate of mercury was 2.36 mg sec^{-1} in all cases. At potentials more cathodic than −1.1 V *vs.* S.C.E., O_2 is reduced to

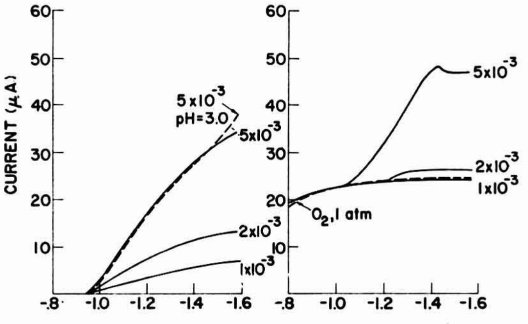


Fig. 1. Polarograms (maximal currents during drop life t_D = 3.1 sec) of Ni^{2+} ions in 0.5 moles/l Na_2SO_4, pH = 5.1 Concn. Ni^{2+} given in moles/l. Left: air-free; dashed line, pH adjusted to 3.0. Right: solution saturated with 1 atm O_2; pH = 5.1; dashed line, $[Fe^{2+}]$ = 0.

OH^- ions quantitatively, no H_2O_2 being formed[18]. The presence of O_2 in the solution of Fe^{2+} did not oxidize any measurable amount ($< 0.1\%$) of this ion during the time of contact (10 min). No Fe^{3+} could be detected polarographically immediately after the runs. The fact that the Ni^{2+}-polarogram (air-free) is stretched out and does not reach the limiting current is in good agreement with recent work[14]. It should be noted here that similar experiments were carried out in other electrolytes ($NaClO_4$, KNO_3, NaCl, K_2SO_4). No significant differences were observed except that in non-complexing 1–1 electrolytes ($NaClO_4$, KNO_3) strong polarographic maxima were obtained in the discharge of Fe^{2+} (O_2 present). The first maximum occurred at −1.1 V while a second maximum was observed at −1.5 V, *i.e.*, at about the normal discharge potential found in the other electrolytes. These maxima could be attributed to the fact that in 1,1 electrolytes the precipitation of the hydroxide is slower than that in 1–2 electrolytes — a rather common observation in colloid chemistry.

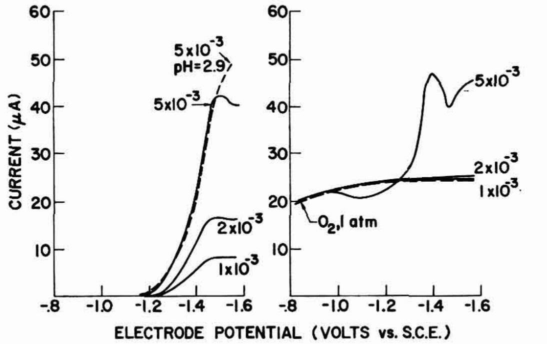


Fig. 2. Polarograms (maximal currents during drop life $t_D = 3.1$ sec) of Co^{2+} ions in 0.5 moles/l Na_2SO_4, pH = 5.0. Concn. Co^{2+} given in moles/l. Left: air-free; dashed line, pH adjusted to 2.9. Right: solution saturated with 1 atm O_2; pH = 5.0; dashed line, $[Co^{2+}] = 0$.

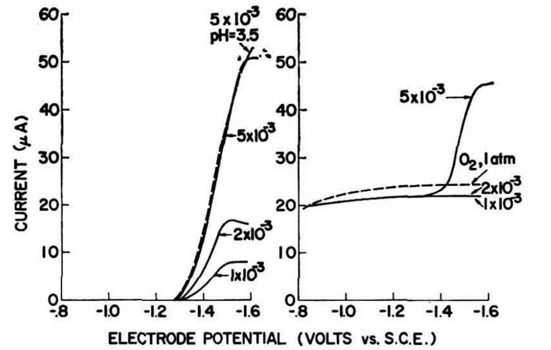


Fig. 3. Polarograms (maximal currents during drop life $t_D = 3.1$ sec) of Fe^{2+} ions in 0.5 moles/l Na_2SO_4, pH = 5.3 Concn. Fe^{2+} given in moles/l. Left: air-free; dashed line, pH adjusted to 3.5. Right: solution saturated with 1 atm O_2; pH = 5.3; dashed line, $[Ni^{2+}] = 0$.

The co-deposition of the three binary systems was measured under identical conditions (Figs. 4–6). It can be seen that in air-free solutions (left-hand diagrams)

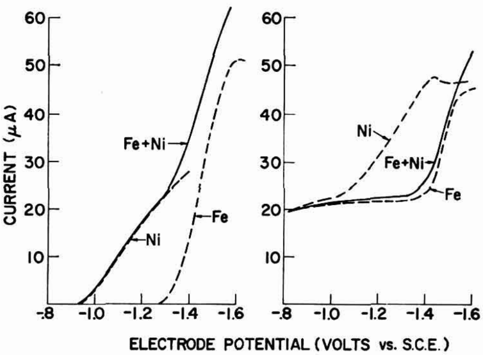


Fig. 4. Polarograms (maximal currents during drop life $t_D = 3.1$ sec) of $5 \cdot 10^{-3}$ moles/l Fe^{2+} and $5 \cdot 10^{-3}$ moles/l Ni^{2+} (separate polarograms, dashed lines; composite polarogram, full line). Left: air-free. Right: solution satd. with 1 atm O_2.

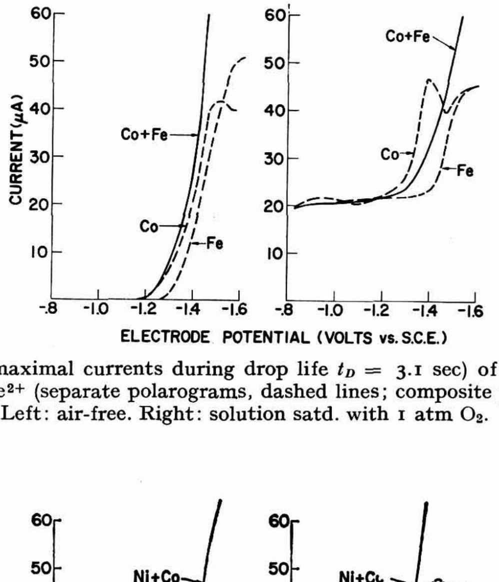


Fig. 5. Polarograms (maximal currents during drop life $t_D = 3.1$ sec) of $5 \cdot 10^{-3}$ moles/l Co^{2+} and $5 \cdot 10^{-3}$ moles/l Fe^{2+} (separate polarograms, dashed lines; composite polarogram, full line). Left: air-free. Right: solution satd. with 1 atm O_2.

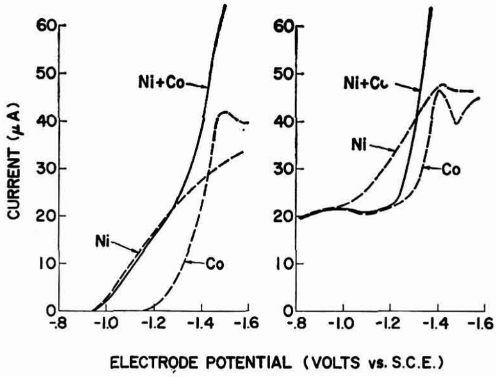


Fig. 6. Polarograms (maximal current during drop life $t_D = 3.1$ sec) of $5 \cdot 10^{-3}$ moles/l Ni^{2+} and $5 \cdot 10^{-3}$ moles/l Co^{2+} (separate polarograms, dashed lines; composite polarogram, full line). Left: air-free. Right: solution satd. with 1 atm O_2.

the discharge reactions proceed without interfering with each other. However, in solutions containing O_2 strong interference is observed in all cases. The presence of ferrous ions causes the strongest suppression in the discharge of the other metals. In all three binary systems the suppression is in the sequence $Fe^{2+} > Co^{2+} > Ni^{2+}$.

In order to evaluate the influence of metal hydroxide on the discharge of ions that do not themselves hydrolyse, the depression of Tl^+ discharge was determined in the presence of hydroxides (Table 1).

TABLE 1

DEPRESSION OF Tl^+ DISCHARGE DUE TO HYDROLYSIS OF IRON-GROUP METALS

Metal ion present	*Hydrolysis current $O_2 \rightarrow OH^-$ (μA)*	*Tl^+ discharge in absence of hydrolysis (μA)*	*Tl^+ discharge in presence of hydrolysis (μA)*	*Depression of current (%)*
$5 \cdot 10^{-3}$ *M* Fe^{2+}	20	70	49	30
$5 \cdot 10^{-3}$ *M* Co^{2+}	21	70	65	7
$5 \cdot 10^{-3}$ *M* Ni^{2+}	23	70	69	1
$5 \cdot 10^{-3}$ *M* $Fe^{2+} + 5 \cdot 10^{-3}$ *M* Ni^{2+}	23	70	52	26
$5 \cdot 10^{-3}$ *M* $Co^{2+} + 5 \cdot 10^{-3}$ *M* Fe^{2+}	20	70	51	27
$5 \cdot 10^{-3}$ *M* $Ni^{2+} + 5 \cdot 10^{-3}$ *M* Co^{2+}	21	70	64	9

All measurements at $E_{S.C.E.} = -1.1$ V; supporting electrolyte, 0.5 *M* Na_2SO_4; pH = 5.1; Tl^+ concn., 0.014 moles/l; $m = 2.36$ mg sec^{-1}; $t_D = 3.1$ sec.

The adsorption of $Fe(OH)_2$ was determined by means of galvanostatic charging curves (Fig. 7). Measurements of this kind have to be carried out quickly in order that no additional reacting material $[Fe(OH)_2]$ can diffuse to and adsorb at the electrode. This point was checked by carrying out the same experiments ten times more rapidly (anodic current density ten times higher). These experiments yielded the same results within ± 10%. It can be calculated from Fig. 7 that the amount adsorbed is 33 ± 2 μC/cm² or $3.3 \pm 0.2 \times 10^{-10}$ moles/cm² respectively.

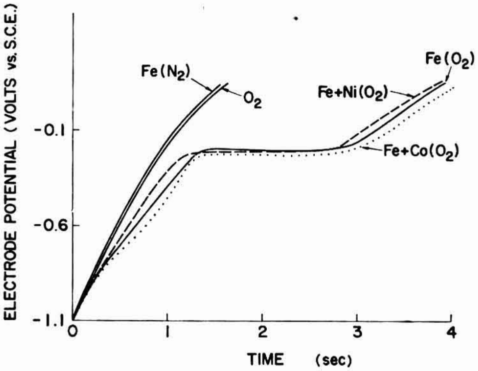


Fig. 7. Potential–time curves at constant anodic current density, 20 mA/cm². Drop life of mercury, 5 sec; rate of mercury flow, 0.99 mg sec^{-1}; electrolyte, 0.5 *M* Na_2SO_4, pH = 5.1. Curves from left to right: (1), $5 \cdot 10^{-3}$ moles/l Fe^{2+}, air-free; (2), satd. with 1 atm O_2, $[Fe^{2+}] = 0$; (3), $5 \cdot 10^{-3}$ moles/l Fe^{2+} and $5 \cdot 10^{-3}$ moles/l Ni^{2+}, satd. with 1 atm O_2; (4), $5 \cdot 10^{-3}$ moles/l Fe^{2+}, satd. with 1 atm O_2; (5), $5 \cdot 10^{-3}$ moles/l Fe^{2+} and $5 \cdot 10^{-3}$ moles/l Co^{2+}, satd. with 1 atm. O_2.

DISCUSSION

It can be seen from Fig. 1–3 (left-hand side) that in weakly acid solutions the pH does not affect the discharge of the iron-group metals ($3 < \mathrm{pH} < 5.5$). This means that the *electrochemical reaction order* (VETTER[19]) of hydrogen ions and hydroxyl ions (Z_{H^+,OH^-}) = 0. For nickel, this observation is in agreement with the mechanism postulated by DANDOY AND GIERST[14].

In order to represent the processes leading to hydrolysis in a simplified form, we will use the concept of a reaction zone at the electrode surface which is separated from the bulk of the solution by a *diffusion bridge*[20]. Since part of the hydrolysis is taking place *on* the *diffusion bridge* this model is simplified, but will be sufficient here. Figure 8 shows the processes involved.

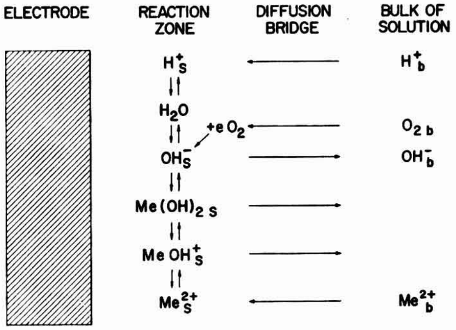


Fig. 8. Schematic representation of hydrolysis processes.

Considering the processes represented in Fig. 8 we can neglect the diffusion of $MeOH^+$, since $[MeOH^+] \ll [Me^{2+}] + [Me(OH)_2]$ at all pH values as follows from the first[20–23] and second[24] hydrolysis constants of all three metals. This does not necessarily imply that $MeOH^+$ does not play a role in the discharge mechanism (see below).

No appreciable fraction of the generated hydroxyl ion is neutralized by indiffusing hydrogen ions under our experimental conditions (pH ~ 5), *i.e.*

$$kD_{H}^{\frac{1}{2}}([H_b^+] - [H_s^+]) \ll kD_{OH}^{\frac{1}{2}}([OH_s^-] - [OH_b^-]) \tag{1}$$

where k is the constant of the Ilkovič equation[26]; D, the diffusion coefficients in $cm^2\,sec^{-1}$; $[H_b]$, $[H_s]$, $[OH_s]$, $[OH_b]$, the concentration of hydrogen ions and hydroxyl ions in the bulk solution and on the surface of the electrode in mmoles/l. Therefore the generated hydroxyl ions will be consumed only by the reaction $2\,OH^- + Me^{2+} = Me(OH)_2$. Hence, the limiting current of metal discharge will be decreased according to

$$i_{Me^{2+}} = kD_{Me^{2+}}^{\frac{1}{2}}[Me^{2+}] - kD_{O_2}^{\frac{1}{2}}\,[O_2] \tag{2}$$

where $i_{Me^{2+}}$ is the current due to discharge of metal ions in μA, and $[Me^{2+}]$ and $[O_2]$ are the concentrations of these species in mmoles/l.

Equation (2) is, of course, based on the assumption that the metal hydroxide which has been formed does not take part in the transfer reaction. According to eqn. (2) the decrease in the limiting current of metal discharge should be equal to the OH^- generating current. It can be seen from Figs. 1–3 that the experimental results are in agreement with eqn. (2) within ± 20%.

In the case of Fe^{2+} hydrolysis, part of the metal hydroxide formed is adsorbed at the electrode surface (Fig. 7). The redox potential of the adsorbed species is $E = -0.20$ V *vs.* the saturated calomel electrode, *i.e.*, $E_H = +0.05$ V in the normal hydrogen scale. The redox potential of the reaction $Fe(OH)_2 + OH^- = Fe(OH)_3 + e$ at pH 8 can be calculated[25] to be at $E_H = -0.19$ V. Since there is no information on the adsorption energies of the species involved or on the modification of iron hydroxide formed, a close agreement should not be expected.

We have to consider how the adsorption of hydrolysed species influences the rate of metal discharge. The rate constants of metal discharge can be calculated following KOUTECKÝ's treatment[26]. In a first approximation, the data obtained in the presence of hydroxide can be treated in the same way, taking the diffusion currents from eqn. (2). The rate constants are plotted in Fig. 9. There is no systematic change in rate constant with hydrolysis. It should be noticed that the change in rate constant is rather small, *i.e.*, there is no evidence for a new rate-determining step under these conditions.

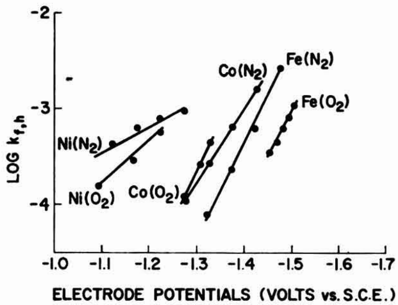


Fig. 9. Rate constant of metal discharge as a function of electrode potential. Supporting electrolyte 0.5 *M* Na_2SO_4; pH, 5.0–5.3; $Me(N_2)$, $5 \cdot 10^{-3}$ moles Me^{2+}/l, solution air-free; $Me(O_2)$, $5 \cdot 10^{-3}$ moles Me^{2+}/l, solution satd. with 1 atm O_2.

The relatively small changes in the rate constant with hydrolysis in the case of single metal discharge are in contrast to the significant changes observed in the simultaneous discharge of the metals (Figs. 4–6). For example, the discharge of nickel is suppressed completely in the presence of ferrous hydroxide (Fig. 4). The effect in suppressing the discharge of other metals can be expressed by the series $Fe^{2+} > Co^{2+} > Ni^{2+}$ for all binary systems. The same sequence is followed for hindering the discharge of Tl^+ ions (Table 1).

In order to interpret this sequence it can be assumed that in mixtures of two hydrolysed metal ions the structure of the interface is determined by the metal having the stronger suppression effect, *e.g.*, in a solution containing Fe^{2+} and Ni^{2+}, it is determined by Fe^{2+}. This hypothesis is in agreement with the observation (Fig. 7) that the presence of other metal ions (Ni^{2+}, Co^{2+}) does not change the amount of adsorbed $Fe(OH)_2$. It explains also the effects of mixtures of two hydrolysed metal species on the discharge of Tl^+ ions (Table 1); *e.g.*, in the presence of both Fe^{2+} and Ni^{2+} ions, the discharge of Tl^+ is suppressed to about the same extent as it is in the presence of Fe^{2+} ions alone.

SUMMARY

The deposition and co-deposition of iron(II), cobalt(II) and nickel(II) ions were studied polarographically in weakly acid (pH 3–5.5) solutions. Variation of pH in this region does not affect the waves. By adding oxygen to the solution, high pH values were generated at the electrode surface ($O_2 + 2\ H_2O + 4\ e \rightarrow 4\ OH^-$) leading to hydrolysis of the discharging metal ions. Hydrolysis not only reduces the concentration of the discharging species due to $Me^{2+} + 2\ OH^- \rightarrow Me(OH)_2 \downarrow$ but also leads to adsorption of hydroxides at the interface. Chronopotentiometric measurements showed that about $3 \cdot 10^{-10}$ moles/cm² $Fe(OH)_2$ are adsorbed at the electrode. Hydrolysis changes the rate of single metal discharge only slightly, but has a strong effect on the co-deposition of metals. The discharge of one metal can be suppressed by the presence of a second iron-group metal. Ferrous ions cause the strongest suppression followed by cobaltous ions. The same sequence ($Fe^{2+} > Co^{2+} > Ni^{2+}$) is found in the suppression of Tl^+ discharge. This sequence is interpreted on the basis of adsorption measurements.

REFERENCES

1 H. FISCHER, *Elektrolytische Abscheidung und Elektrokristallisation von Metallen*, Springer Verlag, Berlin, 1954, pp. 70, 107, 249.
2 F. FOERSTER AND L. KREUGER, *Z. Elektrochem.*, 33 (1925) 406.
3 H. FISCHER, *loc. cit.*, p. 531.
4 A. K. N. REDDY AND H. WILMAN, *Proc. Indian Acad. Sci., Sect. A*, 58 (1963).
5 J. O'M. BOCKRIS, D. DRAŽIĆ AND A. R. DESPIC, *Electrochim. Acta*, 4 (1961) 325 and references given there.
6 K. E. HEUSLER, *Z. Elektrochem.*, 66 (1962) 177.
7 N. SATO AND G. O. OKAMOTO, *Trans. Japan. Inst. Metals*, 2 (1961) 113.
8 H. FISCHER, *loc. cit.*, p. 249.
9 D. J. MACNAUGHTAN, G. E. GORDAM AND R. A. F. HAMMOND, *Trans. Faraday Soc.*, 29 (1933) 729.
10 H. FISCHER, *loc. cit.*, p. 39.
11 M. FLEISCHMANN AND H. R. THIRSK, *Advances in Electrochemistry and Electrochemical Engineering*, Vol. 3, edited by P. DELAHAY, John Wiley and Sons, Inc., New York, 1963, p. 123.
12 V. F. IVANOV AND Z. A. IOFA, *Dokl. Akad. Nauk SSSR*, 137 (1961) 1149.
13 R. BRDIČKA, *Collection Czech. Chem. Commun.*, 3 (1931) 396.
14 J. DANDOY AND L. GIERST, *J. Electroanal. Chem.*, 2 (1961) 116.
15 I. M. KOLTHOFF AND J. J. LINGANE, *Polarography*, Interscience Publishers, New York, 1952, p. 105.
16 F. P. BOWDEN, *Proc. Roy. Soc. London, Ser. A*, 125 (1929) 446.
17 W. MEHL, M. A. V. DEVANATHAN AND J. O'M. BOCKRIS, *Rev. Sci. Instr.*, 29 (1958) 180.
18 I. M. KOLTHOFF AND J. J. LINGANE, *loc. cit.*, p. 553.
19 K. J. VETTER, *Elektrochemische Kinetik*, Springer Verlag, Berlin, 1961, p. 115.
20 P. RUETSCHI AND G. TRUEMPLER, *Helv. Chim. Acta*, 35 (1952) 1021.
21 F. LINDSTRAND, *Svensk Kem. Tidskr.*, 56 (1944) 282.
22 B. O. HEDSTROEM, *Arkiv Kemi*, 5 (1953) 457.
23 J. A. BOLZAN AND A. J. ARVIA, *Electrochim. Acta*, 7 (1962) 589.
24 F. ACHENZA, *Ann. Chim. Rome*, 49 (1959) 624.
25 F. W. LATIMER, *Oxidation Potentials*, Prentice Hall, New York, 2nd ed., 1952.
26 I. M. KOLTHOFF AND J. J. LINGANE, *loc. cit.*, p. 41.
27 J. KOUTECKÝ, *Chem. Listy*, 47 (1953) 323; *Collection Czech. Chem. Commun.*, 18 (1953) 597.

MESURE DIRECTE DES COEFFICIENTS DE DIFFUSION D'IONS EN SOLUTION AQUEUSE EN PRESENCE D'UN ELECTROLYTE SUPPORT

A. M. BATICLE

Laboratoire d'Electrolyse, Centre National de la Recherche Scientifique, Bellevue (S. et O.) (France)

(Reçu le 24 mars, 1964)

La plupart des méthodes d'analyse ou d'étude de cinétique électrochimiques nécessitent l'emploi d'un électrolyte support, c'est-à-dire la présence dans les solutions aqueuses, en plus des espèces actives étudiées, d'un grand excès d'un électrolyte indifférent. Les coefficients de diffusion sont habituellement évalués à partir de mesures indirectes; courants limites de diffusion polarographiques par exemple, ou autres grandeurs.

La mesure directe à l'aide de la cellule de diffusion à deux ou quatre couches de OEHOLM[1] entraîne l'utilisation des tables de STEFAN[2] ou le mode de calcul de EULER[3]. BODMANN ET WITZGALL[4] ont montré la nécessité de corrections et en ont donné les tables. Cette méthode est donc laborieuse.

Nous proposons dans cet exposé une méthode directe de mesure des coefficients de diffusion que nous avons adaptée à la diffusion d'espèces électrochimiques en milieu électrolyte support.

Un certain nombre de méthodes directes, utilisées pour la diffusion de grosses molécules telles que les protéines, sont basées sur le fait que l'indice de réfraction d'une solution est pratiquement proportionnel à sa concentration. Parmi celles-ci la plus précise est certainement celle de la fente oblique de PHILPOT-SWENSON[5]. On a adapté cette méthode à la diffusion d'ions ou de molécules de plus faibles dimensions. La principale difficulté vient de la faible variation des indices de réfraction dans le domaine de concentration peu élevé l'on a opéré.

Le système étudié a été l'hydroquinone en milieu acide sulfurique normal ou eau pure.

Loi de la diffusion

Lorsqu'on superpose une colonne de solvant pur à une colonne de solution homogène des espèces considérées, ions ou molécules dans ce solvant, ces particules se répandent peu à peu dans le solvant initialement pur, par suite de l'agitation brownienne, et leur diffusion, à travers la surface de séparation des deux liquides, obéit à la loi de Fick:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \qquad (1)$$

dans laquelle C représente la concentration de l'ion étudié, t est le temps, x est la distance d'un point où existe le gradient de concentration, à la surface de séparation initiale prise à l'instant $t = 0$ et D est le coefficient de diffusion supposé constant. Si on peut obtenir à chaque instant t la courbe $\partial C/\partial x = f(x)$ on pourra à l'aide de la surface S de cette courbe et de son ordonnée maximum H tracer la courbe $1/H^2 = g(t)$. Cette courbe est une droite qui permet le calcul de D d'après l'éqn.

$$\frac{1}{H^2} = D\,\frac{4\pi k}{S^2}\,t \tag{2}$$

k représente une constante qui dépend de l'échelle de la courbe et des dimensions géométriques de l'appareil utilisé.

Deux hypothèses ont été faites. D'une part la loi de Fick est valable pour les solutions idéales. On devrait donc introduire les activités et non les concentrations dans le domaine où l'on opère. D'autre part, on a supposé le coefficient de diffusion D constant. Ces deux hypothèses sont justifiées en milieu électrolyte support, ce dernier maintenant la force ionique constante. On en verra la vérification dans la partie expérimentale: la courbe $1/H^2 = g(t)$ est bien une droite ce qui ne saurait être si $D \neq$ cte.

Méthode de la fente oblique de PHILPOT-SWENSON

On utilise la variation de l'indice de réfraction de la solution que l'on suppose proportionnelle à la variation de concentration de la solution.

Nous n'avons pas trouvé de données dans la littérature sur l'indice de réfraction des solutions d'hydroquinone dans l'acide sulfurique et les mesures que nous avons faites sont peu précises pour des concentrations faibles. Mais cette troisième hypothèse se trouve justifiée puisque nous avons bien obtenu les droites théoriques $1/H^2 = g(t)$.

Les solutions sont placées l'une au-dessus de l'autre dans une cellule à faces parallèles. Les rayons lumineux émis par une source horizontale traversent la cellule et sont déviés par les régions où existent des gradients de concentration.

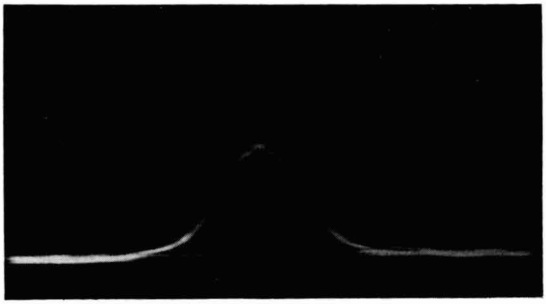


Fig. 1. Image, donnée par l'appareil de Tisélius, de la courbe $\partial C/\partial x = f(x)$.

La superposition d'une lentille sphérique, d'une fente oblique puis d'une lentille cylindrique sur le trajet des rayons lumineux, déviés par la cellule, restitue une image qui est la courbe $\partial C/\partial x = f(x)$ (ref. 5) (Fig. 1).

Appareillage et technique expérimentale

On a utilisé des solutions à 1% et 2% d'hydroquinone dans l'eau pure, et $4 \cdot 10^{-2}$ *M* d'hydroquinone dans H_2SO_4, 0.5 *M*.

Les expériences ont été effectuées à l'aide d'un appareil à électrophorèse de Tisélius (Strübin, Fokal B). La cellule utilisée est représentée sur la Fig. 2. L'élément central, C, et la partie supérieure gauche de la cellule peuvent glisser latéralement sur les plans rôdés (a) et (b), mûs à l'aide d'un piston à air, pour permettre un remplissage séparé des éléments. Au-dessus de (b), dans la branche gauche, on met le solvant pur. Dans la branche droite, le fond E, et l'élément D, est introduite la solution d'hydroquinone. On place alors la cellule dans le thermostat stabilisé à ± 0.2°. L'équilibre de température étant atteint, on fait glisser les plans rôdés de façon à amener les solutions en contact en (b). Cette surface de séparation est alors repoussée dans le milieu du champ optique [milieu de (a), (b)] par une surpression amenée par un excès de solution en F et contrôlée par le capillaire G, le robinet R_2 étant fermé. La durée du déplacement est d'environ 5000 sec, assez lent pour perturber le moins possible la surface de séparation des deux milieux. Puis on ferme les robinets R_1 et R_3.

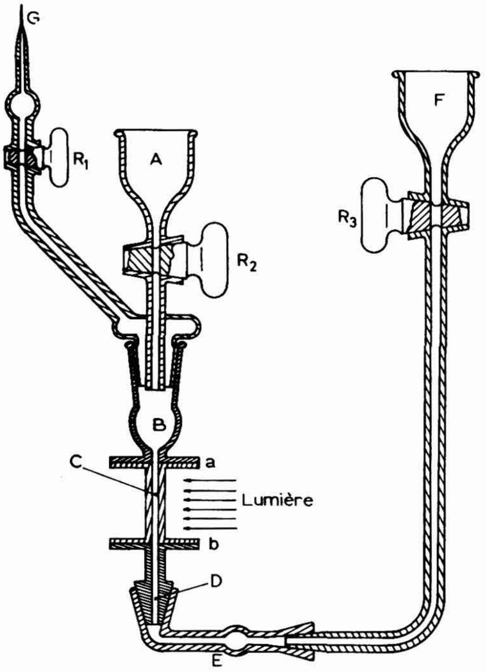


Fig. 2. Cellule de diffusion.

Il importe que les solutions ne supportent aucune vibration. Aussi la mesure se fait en vase fermé. De plus le thermostat est monté sur une suspension antivibratoire et les agitateurs sont attachés sur un bâti étranger au thermostat.

L'image de la courbe $\partial C/\partial x$, obtenue par le système optique de l'appareil de Tisélius, est photographiée toutes les 1000 secondes, pendant 20000 sec. L'erreur introduite par la photographie peut amener une dispersion considérable des résultats.

Il faut obtenir un tracé photographique le plus fin possible tout en gardant une ligne de base bien définie. Il faut éviter la diffraction par les grains du papier sensible. La précision de mesure des grandeurs S et H ainsi que l'évaluation du facteur k de l'éqn. (2) dépendent du tracé photographique. On a été amené à standardiser les conditions d'éclairement et de révélation du film. On a utilisé des microfilms KODAK M 135-36 avec des temps de pose compris entre 10 et 16 sec.

Pour l'appareillage utilisé le terme k de l'éqn. (2) est égal à G^2, G étant le grandissement suivant l'axe des x, dû à l'appareillage et à l'agrandissement photographique. Toutes les courbes $\partial C/\partial x$ sont projetées agrandies et dessinées de façon à mesurer les paramètres H et S.

Résultats expérimentaux

La Fig. 3 montre les courbes $1/H^2 = g(t)$ obtenues pour trois températures pour un même réglage k de l'ensemble expérimental. Les points $1/H^2$ se placent sur des droites.

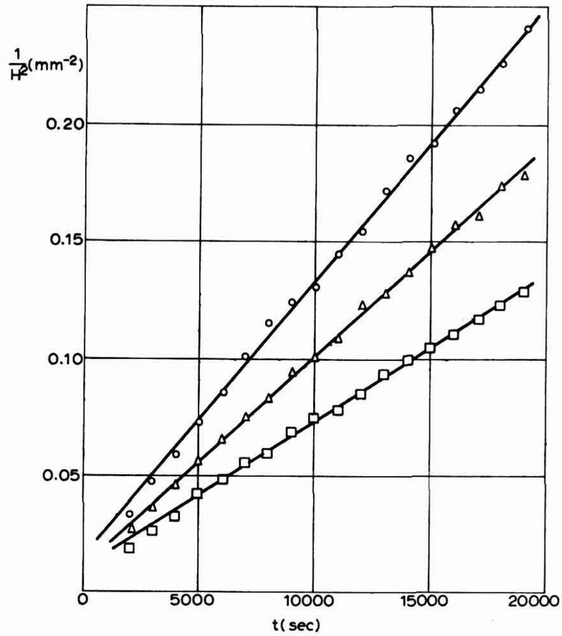


Fig. 3. Courbes $1/H^2 = g(t)$ à trois températures pour un même coefficient k de l'appareillage. $4 \cdot 10^{-2}$ M hydroquinone dans 0.5 M H_2SO_4. $S^2/4\pi k = 0.65$. ○, 20°; △, 15°; □, 2.8°.

On notera la perturbation due au déplacement de la surface initiale qui fait que les premiers points ne sont pas sur la droite. Ce déplacement augmente la vitesse de diffusion et on peut voir que le prolongement de la droite $1/H^2 = g(t)$ coupe l'axe des abscisses en 1 point antérieur au temps $t = 0$.

La variation des indices de réfraction est proportionnelle à la température puisque, pour un même réglage k, nous avons pu obtenir, pour une série d'expériences à 2.8°, 15° et 25°, $\Delta S/S = \pm 1\%$ (température exprimée en degrés centésimaux).

Malgré toutes les précautions prises les photographies ne sont pas parfaitement reproductibles. Le tracé manuel des images agrandies introduit lui aussi une certaine dispersion. Il convient donc de prendre la valeur moyenne de D sur plusieurs essais pour chaque température.

La dispersion des résultats augmente lorsque la température croit et lorsque la dilution de la solution initiale augmente. Nous avons essayé de partir de solutions plus diluées en hydroquinone. Les surfaces des images sont proportionnelles aux concentrations et l'erreur relative augmente quand ces surfaces diminuent.

Pour les solutions à 1% d'hydroquinone dans l'eau pure à 16° nous avons trouvé:

$$D = 6.80 \times 10^{-6}\ \mathrm{cm^2\ sec^{-1}}$$

Pour des solutions $4 \cdot 10^{-2}\ M$ d'hydroquinone dans H_2SO_4 0.5 M nous avons obtenu à différentes températures:

$$2.8^\circ : \mathrm{D} = 4.07 \times 10^{-6}\ \mathrm{cm^2\ sec^{-1}} \pm 0.05$$

$$15^\circ : \mathrm{D} = 5.90 \times 10^{-6}\ \mathrm{cm^2\ sec^{-1}} \pm 0.07$$

$$25^\circ : \mathrm{D} = 7.77 \times 10^{-6}\ \mathrm{cm^2\ sec^{-1}} \pm 0.14$$

Discussion des résultats

On a vérifié que les hypothèses de départ étaient satisfaites. Les courbes $1/H^2 = g(t)$ étant des droites on peut donc remplacer les activités par les concentrations dans la loi de Fick, les coefficients de diffusion sont constants quand la concentrations diminue (lorsque t augmente) et les variations d'indice de réfraction sont proportionnelles aux concentrations.

On n'a pas trouvé de valeurs du coefficient de diffusion de l'hydroquinone dans l'acide sulfurique dans la littérature. KRÜGER ET GRUNSKY[6] ont mesuré le coefficient de diffusion de l'hydroquinone dans l'eau par la méthode de la cellule à couches, solutions à 1% et 2% à 16°. Par un système d'intégrations graphiques ils ont obtenu $D = 6.78 \times 10^{-6}\ \mathrm{cm^2\ sec^{-1}}$. Le calcul d'EULER leur a donné $D = 6.87 \times 10^{-6}\ \mathrm{cm^2\ sec^{-1}}$, valeurs en bon accord avec les valeurs déterminées ci-dessus.

On connait la relation de Stokes–Einstein pour la diffusion de particules sphériques de rayon r dans un milieu de viscosité η:

$$D = \frac{kT}{6\pi r\eta} \tag{3}$$

dans laquelle k est la constante de Planck et T la température absolue.

Cette relation peut être utilisée pour le calcul des rayons des particules diffusantes. Elle est valable dans le cas de particules sphériques non chargées et dans le cas de certains ions[7,8].

Il semblait intéressant de voir s'il était possible de l'appliquer au système étudié et, dans l'affirmative, d'obtenir des renseignements sur l'état de l'hydroquinone en solution, renseignements qu'on n'a pas acquis dans la littérature.

En prenant pour valeurs de η les viscosités de l'acide sulfurique 0.5 M mesurées par KNIETSCH[9] et en admettant pour la courbe $\eta = f(T)$ une variation analogue à la même courbe pour l'eau, nous avons calculé $D\eta/T$ pour les différentes valeurs de D obtenues:

hydroquinone dans l'eau:

KRÜGER (graph.) 16° : $D\eta/T = 0.259 \times 10^{-9}$
KRÜGER (EULER) 16° : $D\eta/T = 0.262 \times 10^{-9}$
nos expériences 16° : $D\eta/T = 0.260 \times 10^{-9}$

hydroquinone dans H_2SO_4 0.5 *M*:

nos expériences 2.8° : $D\eta/T = 0.258 \times 10^{-9}$
15° : $D\eta/T = 0.257 \times 10^{-9}$
25° : $D\eta/T = 0.259 \times 10^{-9}$

A la précision de nos mesures, 1.1–1.8% sur *D*, le produit $D\eta/T$ est constant. En admettant que la relation de Stokes–Einstein s'applique nous pouvons alors calculer le rayon de la molécule d'hydroquinone ce qui conduit à:

$r = 2.80$ Å dans l'eau

$r = 2.81$ Å dans l'acide

Ce résultat indiquerait un même état d'hydratation de l'hydroquinone dans l'eau pure et dans l'acide sulfurique 0.5 *M*.

On remarquera que le rayon obtenu est faible pour une molécule de masse relativement élevée. On peut penser que le nombre de molécules d'eau d'hydratation est faible.

En terminant remarquons que la méthode de la fente oblique de Philpot-Swenson, utilisée habituellement pour des coefficients de diffusion de l'ordre de 10^{-7}–10^{-6} cm^2 sec^{-1} a permis la mesure de coefficients *D* de l'ordre de 10^{-6}–10^{-5} cm^2 sec^{-1}. On peut voir néanmoins que la précision diminue quand la température augmente, c'est-à-dire quand la vitesse de diffusion augmente. On peut espérer toutefois étudier un grand nombre de systèmes par ce moyen, puisque beaucoup d'ions ont des vitesses de diffusion de cet ordre.

Comme l'ont montré, à la fois, l'analyse du principe de la méthode et les résultats expérimentaux, cette détermination des coefficients de diffusion est particulièrement bien adaptée au cas des solutions électrochimiques en milieu électrolyte support, la présence d'un grand excès d'électrolyte indifférent permettant de satisfaire aux hypothèses nécessaires. Une restriction s'impose toutefois; il faut obtenir une variation d'indice de réfraction suffisante pour que les images soient nettes et assez grandes pour être précises. Ceci limite la dilution des espèces actives en solution.

REMERCIEMENTS

L'auteur remercie Madame J. DE MENDE et Monsieur D. ROLLAND du Centre d'Electrophorèse du C.N.R.S. pour leur collaboration technique.

RÉSUMÉ

On a adapté la méthode de la fente oblique de Philpot-Swenson à la mesure des coefficients de diffusion d'ions ou de molécules en solutions contenant un excès d'électrolyte support. Les essais ont été réalisés pour l'hydroquinone en milieu acide sulfurique 0.5 *M*.

La dispersion des mesures varie de 1.2–1.8% entre 2.8° et 25°.

La relation de Stokes–Einstein s'applique au système étudié.

SUMMARY

Philpot-Svenson's oblique slit method for the measurement of the diffusion coefficients of ions or molecules in solutions containing an excess of supporting electrolyte has been adapted. The tests were carried out for hydroquinone in 0.5 *M* sulfuric acid.

The scatter of the measurements varies from 1.2 to 1.8% between 2.8 and 25°.

The system studied follows the Stokes-Einstein relation.

BIBLIOGRAPHIE

1 L. W. Oeholm, *Medd. Nobel Inst.*, 2 (1912) 22.
2 J. Stefan, *Sitzber. Akad. Wiss. Wien, Math. naturw. Kl. Abt. II*, 79 (1879) 161.
3 H. V. Euler, A. Hedelius et O. Svanberg, *Z. Physiol. Chem.*, 110 (1920) 190.
4 O. Bodmann et C. Witzgall, *Z. Physik. Chem. Frankfurt*, 36 (1963) 148.
5 J. Tonnelat, *Traité de Biochimie Générale*, Tome I, Masson et Cie, Paris, 1959, p. 801.
6 D. Krüger et H. Grunsky, *Z. Physik. Chem. Leipzig*, A 150 (1930) 115.
7 M. C. Petit, *Electrochim. Acta*, 8 (1963) 217.
8 I. M. Kolthoff et J. J. Lingane, *Polarography*, Interscience Publishers Inc., New York, 1941.
9 Knietsch, *Rev. Gén. Chim.*, I (1902) 65.

EFFECTS OF ANIONS AND CATIONS ON OXYGEN REDUCTION AND OXYGEN EVOLUTION REACTIONS ON PLATINUM ELECTRODES

AKIYA KOZAWA*

Department of Chemistry, Western Reserve University, Cleveland 6, Ohio (U.S.A.)

(Received March 16th, 1964)

INTRODUCTION

It has been well recognized in the past ten years that the platinum electrode is not inert and that the surface is electrochemically oxidized and reduced in aqueous solutions[1-4]. The electrode surface is covered with oxide film and/or an adsorbed oxygen layer in a certain potential range and the oxide films play an important role in various electrochemical reactions on the platinum electrodes[5-8]. Various metal oxides with hydrated surfaces usually exhibit ion-exchange adsorption in aqueous solutions, that is, a cation-exchange adsorption in alkaline solutions and an anion-exchange adsorption in acid solutions[9]. Cation-exchange adsorption on manganese dioxide and silica has been studied and formation of a surface complex as a new adsorption mechanism was proposed by the author[10,11]. Since the platinum electrode is covered with an oxide film, cations should be adsorbed in alkaline solutions and anions in acid solutions, on the electrode surface. In view of such an ion-exchange adsorption, cations and anions added to the electrolyte should affect oxygen reduction and oxygen evolution reactions at platinum electrodes. In this paper the effects of anions and cations added to 1 *M* NaOH or 1 *N* H_2SO_4 on the oxygen reduction and oxygen-evolution process will be described.

Electrochemical reduction of oxygen at platinum electrodes in alkaline or acid solutions has been studied by voltammetry[12-14], and chronopotentiometry[13,15]. The reaction is very much influenced by the surface condition of the platinum electrode. LAITINEN AND KOLTHOFF[12] and later, SAWYER AND INTERRANTE[13], reported that the half-wave potential of oxygen reduction on platinum is independent of the pH of the solution at pre-cathodized electrodes, but changes linearly with a slope of approximately −60 mV per pH unit at pre-oxidized electrodes. For the mechanism of oxygen reduction, the following three processes are frequently considered in discussions[12-15] (see p. 21).

Although these equations are written for alkaline solution and the $E_{\mathrm{red}}°$ values are for alkaline solution, the corresponding equations for acid solution can easily be written. In the first mechanism**, oxygen is reduced directly to OH^- by a four-

---

* Present address: Research Laboratory, Union Carbide Corporation, Consumer Products Division, Parma 30, Ohio, U.S.A.

** This is ordinarily considered as an over-all reaction, it could, however, be considered as a mechanism in those circumstances where no particular intermediate is recognized experimentally.

electron transfer process. This mechanism was supported with data obtained by BOCKRIS AND HUQ[16] in highly purified 0.1 ~ 0.001 N H_2SO_4; they pointed out that the exchange current for the reaction was so small that the reversible potential corresponding to eqn. (1) could be obtained only in highly purified solutions. In the

$$O_2+2\,H_2O+4\,e \rightleftharpoons 4\,OH^- \qquad E_{\mathrm{red}}^{\circ}=+0.401 \tag{1}$$

$$\begin{tikzcd} \mathrm{Pt}+\frac{1}{2}O_2+H_2O \arrow[r, "\text{chemical}"] & \mathrm{Pt(OH)_2} \arrow[dl] \\ \mathrm{Pt(OH)_2}+2\,e \rightleftharpoons \mathrm{Pt}+2\,OH^- & \end{tikzcd} \qquad E_{\mathrm{red}}^{\circ}=+0.155^{36} \tag{2}$$

$$\begin{tikzcd} O_2+H_2O+2\,e \rightleftharpoons OOH^-+OH^- & \\ OOH^- \arrow[r, "\text{chemical}"] & \frac{1}{2}O_2+OH^- \arrow[ul] \end{tikzcd} \qquad E_{\mathrm{red}}^{\circ}=-0.076 \text{ or } -0.05^{52-54} \tag{3}$$

second mechanism, the platinum surface is oxidized chemically by dissolved oxygen, the platinum hydroxide (or adsorbed oxygen) is then reduced electrochemically[12,15]. Comparing the observed half-wave potentials[12,14] with the $E_{\mathrm{red}}^{\circ} = +0.155$ V, this mechanism is acceptable from a thermodynamic standpoint. The third mechanism was proposed by BERL[17] based on his experiments with carbon electrodes. Later YEAGER *et al.*[18] showed by using ^{18}O that a bond between the atoms in O_2 is not broken in the electrochemical reduction on carbon. Until last year the only support for this mechanism on platinum electrodes was a qualitative detection of hydrogen peroxide by LAITINEN AND KOLTHOFF[19] and a quantitative determination of hydrogen peroxide by DELAHAY, who carried out the oxygen reduction experiments in 0.2 N KCl solution (pH 6.9) on various metals and determined hydrogen peroxide in the solution by a polarographic method[20]. Recently the author[21] has measured the coulombic efficiency for H_2O_2 formation in O_2 reduction on platinum in acid and alkaline solutions. Of the three mechanisms, only (3) involves hydrogen peroxide as a product. The effects of anions and cations on the formation of hydrogen peroxide in oxygen reduction on platinum have been examined mainly in 1 M NaOH[22]. In the present experiments, the coulombic efficiency for hydrogen peroxide formation has been determined in 1 N H_2SO_4 as well as 1 M NaOH, with and without added cations and anions.

Oxygen overvoltage has been reviewed by BREITER[23]. It was demonstrated by means of ^{18}O-labelled anions that the oxygen-evolution reaction at smooth platinum electrodes involves anions, at least in high concentrations (5.8–10 N) of $HClO_4$[24] and H_2SO_4[25]. HICKLING AND HILL[26] reported that oxygen overvoltage at a smooth platinum electrode increased by 10–60 mV in 1 M KOH and 40–180 mV in 1 N H_2SO_4 in the presence of 0.02 M KF. ERDEY-GRÚZ AND SHAFARIK[27] showed that oxygen overvoltage on smooth platinum in 1 N H_2SO_4 increased in the presence of large amounts (0.3 ~ 1.0 M) of cations in the following order: $K^+ > Al^{3+} > NH_4^+ > Zn^{2+} > Na^+ > Mg^{2+} > Li^+$. There seems to be no data on the effect of alkaline-earth metal cations on oxygen overvoltage in alkaline solution. It will be shown in this paper that oxygen overvoltage in 1 M NaOH increased by 15 ~ 90 mV in the presence of 10^{-4}–10^{-2} M of Ba^{2+}, Sr^{2+}, Ca^{2+} on platinum and other metal electrodes.

In the potential range involved in the oxygen-reduction and oxygen-evolution reactions on the platinum electrode, the electrode surface is covered with oxide film. Therefore, a knowledge of the surface condition of platinum in terms of oxide film and/or adsorbed oxygen is necessary in order to interpret the experimental results. For this purpose a brief summary on the adsorbed hydrogen, adsorbed oxygen and oxide films on anodized- and cathodized-platinum electrodes will be given. Some details will be given of an oxide film formed on an excessively anodized platinum electrode in H_2SO_4 solution, since this oxide film has not often been described previously.

EXPERIMENTAL

Oxygen reduction experiments were carried out in an ordinary polarographic H-cell with a fritted-glass layer in the centre. For coulombic efficiency measurements, 25 ml of 1 M NaOH or 1 N H_2SO_4 solution was put in to each arm of the H-cell. A rectangular platinum electrode of 16 or 18 cm² apparent surface area was placed as a cathode in the solution in one arm, where pure oxygen gas (1 atm) was bubbled through the solution during the experiments; another small platinum electrode (1 cm² apparent surface area) was placed in the other arm as an anode. A constant current (1.0 mA in most of the experiments) was passed between the anode and the cathode for a measured time, usually 2–20 min. A portion of the cathode solution (usually 20.0 ml) was taken out and acidified in the case of 1 M NaOH solution, and the hydrogen peroxide concentration was determined by a spectrophotometric method. The method[21] is based on the formation of a yellow colour[28] in the reaction between H_2O_2 and $TiCl_4$ in 6 N HCl. By this method 5–100 μg of H_2O_2 in a 30-ml solution could be determined within an error of a few per cent when a 10-cm cell was used in the extinction measurements.

Solutions were prepared from triply-distilled water. Sulfuric acid was purified by distillation twice in a current of air at about 210°. The 1 M NaOH solution was purified by pre-electrolysis at a platinum cathode under a nitrogen atmosphere for at least 30 h. Various salt solutions which were added to 1 M NaOH or 1 N H_2SO_4 solutions were prepared from chemicals of analytical-reagent grade without further purification. Decomposition of hydrogen peroxide in these purified solutions was negligible for 10–20 min in the absence of a platinum electrode.

Two types of platinum electrode were used; one was pre-cathodized and the other pre-anodized in 1 M NaOH or 1 N H_2SO_4 depending on the solution used for the oxygen reduction experiments. The cathodic or anodic treatment was carried out for about 20 sec at a current density of 5 mA/cm² immediately before use. As will be discussed later, during most of the oxygen reduction experiments the pre-anodized electrode is probably covered with PtO_2-film in both acid and alkaline solutions, and the pre-cathodized electrode covered at least partially with $Pt(OH)_2$ or a similar oxide in 1 N NaOH solutions saturated with oxygen. It is a common experience that the "activity" of platinum electrodes depends on the history and the pre-treatment of the electrodes. In the preliminary experiments, a few electrodes were etched in a hot *aqua regia* solution or treated in a boiling 6 N HCl solution, or treated anodically and cathodically alternately, and then finally anodized or cathodized as mentioned above immediately before the coulombic efficiency measurements. The efficiencies of the anodized electrodes, were not much different. Large differences occurred with the cathodized electrodes particularly in alkaline solutions; however, the relative effects of added anions and cations were the same with these electrodes. In this paper, therefore, a series of experiments shown in any one table or figure has usually been carried out with the same electrode at our time. Furthermore, in the experiments to examine the effect of anions or cations, the electrode was tested before and after each experiment in a standard solution without additives to show that there had been no permanent change in the electrode.

Current–potential curves for the oxygen reduction and oxygen-evolution processes were measured polarographically in the H-cell mentioned above. In these measurements, a small platinum electrode was placed in a solution stirred by O_2 in one arm of the H-cell and a mercurous sulfate plus 1 *N* H_2SO_4 (+0.667 V *vs.* N.H.E.) or a mercuric oxide plus 1 *M* NaOH (+0.115 *vs.* N.H.E.) electrode was placed in the other arm. These reference electrodes, which were also used in these experiments as counter electrodes, were not polarized more than a few millivolts even when 50–100 μA was drawn. All the potentials in this paper are expressed against N.H.E. and all the experiments described were carried out at room temperature which was about 25°.

RESULTS AND DISCUSSION

1. Surface condition of platinum electrodes

(a) Anodized or cathodized electrode. It was shown previously by the author[3,29] and other investigators[2] that current–potential curves of platinum electrodes taken between hydrogen evolution and oxygen evolution potentials in an aqueous solution saturated with inert gas gave a series of peaks due to reduction or formation of

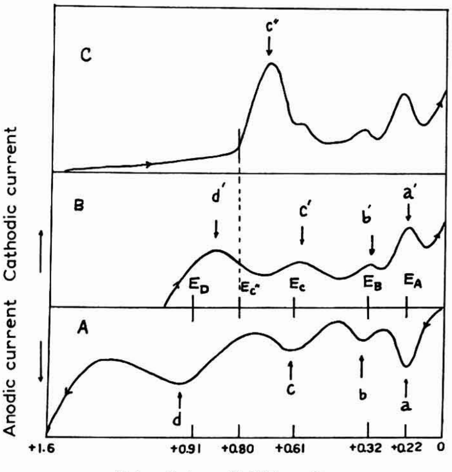


Fig. 1. Schematic current–potential curves of platinum electrodes. (A), oxidation curve taken at a cathodized electrode from negative to positive potentials; (B), reduction curve taken at a cathodized electrode from 1.0 V to negative potential; (C), reduction curve taken at an anodized electrode from positive to negative potentials.

adsorbed hydrogen and platinum oxides or adsorbed oxygen. A schematic summary of these curves of an anodized or a cathodized platinum electrode is shown in Fig. 1. The original curves were taken in 1 M NaOH[3] with a potential scanning rate of 2.5 mV/sec and these curves were then shifted to those in a solution of $a_{H^+} = 1$ by assuming that the peaks moved exactly -59 mV/pH unit. The presence of four peaks (a,b,c,d) on the oxidation curve A and four peaks (a',b',c',d') on the reduction curve B, indicates that four redox couples A,B,C, and D exist on the surface of platinum electrodes. From the centre of the two conjugated peak potentials (a,a'; b,b'; etc.), approximate standard redox potentials E_A,E_B,E_C, and E_D were obtained and shown on the abscissa. It has been interpreted that the redox couples A and B are two forms of adsorbed hydrogen[3,30-35]; the redox couple C was not observed in 1 N H_2SO_4[2,3] and has not yet been identified, and the redox couple D is adsorbed oxygen and/or platinum hydroxide ($Pt(OH)_2$). On the reduction curve of the anodized electrode (curve C), peak (d') was not observed but peak (c″) appeared at a more cathodic potential than (d'). It was interpreted that the anodized electrode was covered with $PtO_2 \cdot n\,H_2O$ and the hydrated platinum dioxide film was reduced directly to Pt at peak (c″)[3], by comparing the potential with the following value[36,37]:

$$PtO_2 \cdot n\,H_2O + 4\,H^+ + 4\,e \rightleftharpoons Pt + (n+2)\,H_2O \qquad E_{red}^\circ = +0.80 \tag{4}$$

(b) Excessively anodized electrode. A new oxide film, which was not involved in the discussion above, was found on the surface of a platinum electrode which was excessively anodized in H_2SO_4. A platinum-wire electrode (apparent area, 0.53 cm²) was polished with fine emery in each case before the anodic treatment. It was then

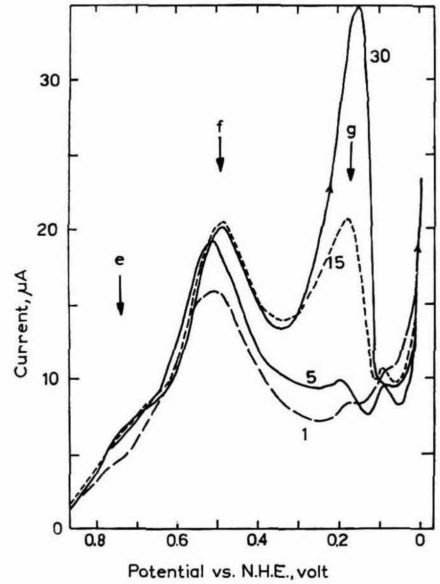


Fig. 2. Effect of electrolysis time. The anodization was carried out at 100 mA/cm² in 1 N H_2SO_4 at 25°. The numbers 1, 5, 15, and 30 are the electrolysis times in min of the anodization.

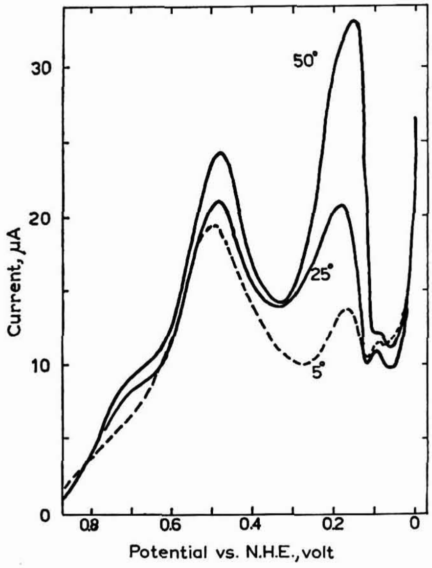


Fig. 3. Effect of temperature. The anodization was carried out at 100 mA/cm² for 15 min in 1 N H_2SO_4 at the temperatures indicated.

anodized under various conditions as described in Figs. 2, 3, 4, 5, and 6, and current–potential curves were taken in N_2-saturated 1 N H_2SO_4 at 25° from +0.87 V towards a negative potential at 3 mV per sec in the same manner as described previously[3]. It can be seen in Figs. 2–6 that there are three peaks (e, f, g) on these curves. We can see that the peak (f) remains almost unchanged regardless of the conditions of

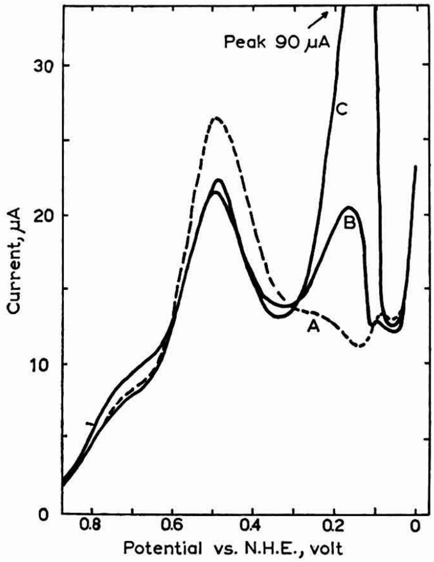


Fig. 4. Effect of current density. The anodization was carried out in 1 N H_2SO_4 for 15 min at 25° at the following current densities: (A), 30 mA/cm²; (B), 100 mA/cm²; (C), 300 mA/cm².

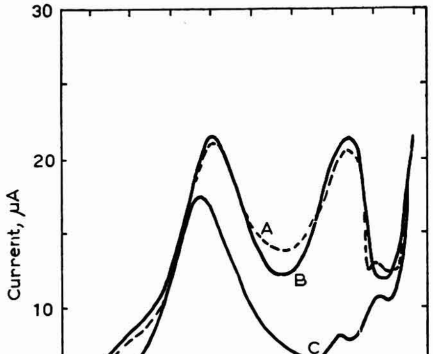


Fig. 5. Effect of the electrolyte solution. The anodization was carried out at 100 mA/cm² for 15 min at 25° in 1 N H_2SO_4 (curve A), 0.1 N H_2SO_4 (curve B), and 1 M NaOH (curve C).

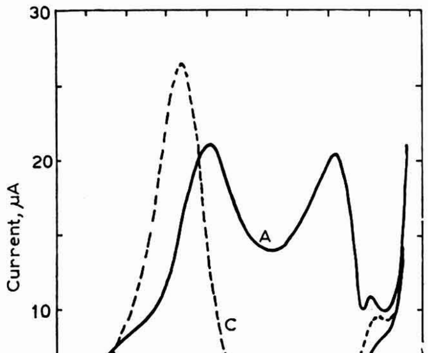


Fig. 6. Curves taken consecutively. (A), 1st curve after the anodization at 100 mA/cm² for 15 min in 1 N H_2SO_4 at 25°; (B), 2nd curve immediately after the 1st curve; (C), taken after the 2nd curve after re-anodizing at 100 mA/cm² for 1 min in 1 N H_2SO_4 at 25°.

the anodizing; however, peak (g) increases with increasing anodizing time (Fig. 2), temperature of the solution (Fig. 3), and current density (Fig. 4) in the anodic treatment. The anodic treatment in 1 *M* NaOH did not show peak (g), see Fig. 5. Peak (g) appears in the same potential range as that of the peak (b) which is due to formation of adsorbed hydrogen ($H^+ + e \rightarrow H_{ads}$). A repeat trial without re-anodization shows the normal two peaks for adsorbed hydrogens (Fig. 6) and a third trial after re-anodization (Fig. 6, curve C) shows a curve quite similar to curve C in Fig. 1. Therefore, peak (g) is not due to an enlargement of peak (b), but seems to be due to a new kind of oxide which is formed only by excessive anodic treatment at high current density. Peak (f) reaches a steady state after a few minutes' anodization and does not change on further anodization (Fig. 2). Also, peak (f) is insensitive to temperature and current density in the anodization (Fig. 3, 4). Although peak (f) appears at a little more cathodic potential than peak (c″) (on curve C in Fig. 1) which is due to reduction of $PtO_2 \cdot n\ H_2O$, this might be due to a somewhat more stabilized form of $PtO_2 \cdot n\ H_2O$.

In order to obtain an X-ray diffraction pattern of the new oxide corresponding to peak (g), a platinum plate with a platinum wire lead was anodized at 300 mA/cm^2 for 100 h in 1 *N* H_2SO_4 at 35–45°. A yellow-coloured film appeared after anodization for 3 h, and the colour became deeper with continued electrolysis. Several X-ray diffraction patterns were taken from time to time during the anodization and the only diffraction peaks found were those of platinum metal. This might be due to the amorphous nature of the oxide film. This yellow oxide cannot be attributed to any impurity such as Pb^{2+} or Mn^{2+} which can be deposited as PbO_2 or MnO_2, because the sulfuric acid solution was made of highly purified water and distilled sulfuric acid.

The anodic oxide film on platinum was studied in connection with platinum-foil anodes used in the production of persulfate by electrolysis of a $[H_2SO_4 + (NH_4)_2SO_4]$ solution[38]. A yellow compound formed on an anodized platinum was described by RUER[39] as $Pt(OH)_2SO_4 \cdot 3\ Pt(OH)_4 \cdot PtO_2$. Anodic oxidation of platinum was studied with a.c. superposed on d.c. current by ALTMANN AND BUSCH, who found that $PtO_2 \cdot n\ H_2O$ came off the electrode[40]. Recently SHIBATA[41] found a large step just before the hydrogen evolution on a chronopotentiogram of a heavily anodized platinum electrode. This probably corresponds to the peak (g) described in this paper.

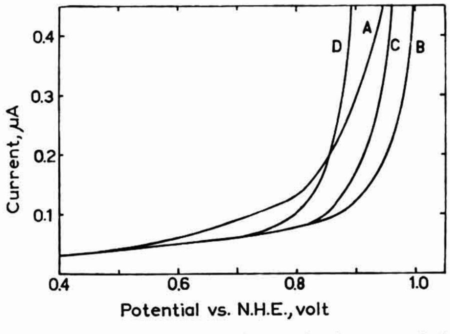


Fig. 7. Current–potential curves of a platinum electrode (0.05 cm^2) in nitrogen-saturated unstirred 1 *N* H_2SO_4. The potential scanning rate was 3 mV/sec. KBr added: (A), 0 *M*; (B), 10^{-3} *M*; (C), 10^{-2} *M*; (D), 10^{-1} *M*.

Oxygen gas containing 15% of ozone by weight was produced at very high current density on a platinum anode in a sulfuric acid solution ($d_{111} = 1.065$)[42]. These informations from the literature indicate that the oxide film corresponding to peak (g) shown in Figs. 2–6 may not be a new oxide, but has not been well recognized.

(c) Effect of Br^-. The effect of bromide ion on the current–potential curves of a platinum electrode in 1 *N* H_2SO_4 saturated with nitrogen is shown in Fig. 7. Curve A in the figure is a process of formation of oxide film and/or adsorbed oxygen on the platinum electrode and this process is inhibited in the presence of small amounts of Br^- (curves B, C, and D). A sharp rise of the current in the curves B, C, and D is due to oxidation of Br^- ion. The results of Fig. 7 suggest that Br^- ion is strongly adsorbed on the platinum surface in 1 *N* H_2SO_4 and prevents electrochemical oxidation of the platinum surface.

2. *Effects of cations and anions on oxygen reduction*

(a) Coulombic efficiency. The effect of various cations and anions on the coulombic efficiency for production of hydrogen peroxide was examined at a constant current of 1.0 mA for an electrolysis time of 10 min at a platinum electrode 16 cm² in area. The results for an anodized platinum electrode are shown in Tables 1 and 2 for 1 *M* NaOH and 1 *N* H_2SO_4, respectively. The efficiency values were calculated on the basis of $O_2+H_2O+2\,e \rightarrow OOH^-+OH^-$ or $O_2+2\,H^++2\,e \rightarrow H_2O_2$. The efficiency values for a cathodized electrode were lower than those (Tables 1 and 2) for an anodized electrode in both acid and alkaline solutions; however, the effects

TABLE 1

EFFECT OF CATIONS IN 1 *M* NaOH

No.	*Electrolyte*	H_2O_2 *formed*[a] (*μg ± 1.2μg*)	*Efficiency* (*%*)
1	1 *M* NaOH	72.0	68.0
2	1 *M* NaOH + 0.001 *M* $CaCl_2$[b]	49.5	46.7
3	1 *M* NaOH + 0.001 *M* $Sr(ClO_4)_2$	38.4	36.2
4	1 *M* NaOH + 0.001 *M* $Ba(ClO_4)_2$	22.4	21.1

[a] By electrolysis for 10 min at a constant current of 1.0 mA at an anodized Pt electrode 16 cm² in area in a 25 ml of solution.
[b] White precipitate, [$Ca(OH)_2$], was in suspension.

TABLE 2

EFFECT OF ANIONS IN 1 *N* H_2SO_4

No.	*Electrolyte*	H_2O_2 *formed*[a] (*μg ± 1.0 μg*)	*Efficiency* (*%*)
5	1 *N* H_2SO_4	15.0	14.2
6	1 *N* H_2SO_4 + 0.033 *M* KF	18.7	17.6
7	1 *N* H_2SO_4 + 0.033 *M* KCl	32.8	30.5
8	1 *N* H_2SO_4 + 0.033 *M* KBr	55.2	52.0
9	1 *N* HCl	39.2	36.9

[a] By electrolysis for 10 min at a constant current of 1.0 mA at an anodized Pt electrode 16 cm² in area in a 25 ml of solution.

of the addition of the anions and cations were relatively the same. Among the various cations and anions tested, only halide ions in acid solution, and alkaline-earth metal ions in alkaline solution showed any marked effect.

So far as the coulombic efficiency for H_2O_2 production in alkaline solution is concerned, ClO_4^-, NO_3^-, CO_3^{2-}, SO_4^{2-}, F^-, Cl^-, Br^-, Zn^{2+} had very little effect up to 3.3×10^{-2} *M*[22]. The marked effect of Ba^{2+}, Sr^{2+}, and Ca^{2+} ions on the efficiency was completely removed by adding EDTA (Na salt of ethylenediaminetetracetate) to the solution[22].

(b) Effect of H_2O_2 decomposition. During the coulombic efficiency measurements, some hydrogen peroxide produced electrochemically may have been decomposed at the electrode as well as in the bulk solution, since platinum is a good catalyst for hydrogen peroxide decomposition[43]. It should therefore be expected that the longer the electrolysis time the greater would be the amount of decomposition. In order to

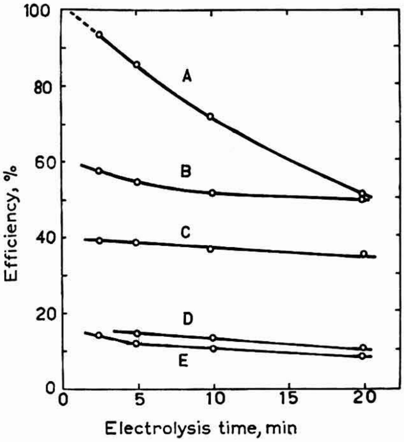


Fig. 8. Efficiency of hydrogen peroxide formation at a pre-anodized platinum electrode for various electrolysis times in the following solutions: (A), 1 *M* NaOH; (B), 1 *N* H_2SO_4 + 10^{-2} *M* KBr; (C), 1 *N* HCl; (D), 1 *M* NaOH + 10^{-2} *M* $Ba(OH)_2$; (E), 1 *N* H_2SO_4.

TABLE 3

PERCENTAGE OF H_2O_2 PRODUCING ELECTROCHEMICAL REACTION ESTIMATED BY EXTRAPOLATION TO ZERO TIME

Electrolyte	*At anodized Pt (%)*	*At cathodized Pt (%)*
1 *N* H_2SO_4	8.5	0.0
1 *N* H_2SO_4 + 10^{-4} *M* Br^-	35.8	39.0
1 *N* H_2SO_4 + 10^{-2} *M* Br^-	51.3	54.5
1 *N* H_2SO_4 + 10^{-1} *M* Br^-	55.7	55.7
1 *M* NaOH	85–100[a]	20–45[a]
1 *M* NaOH + $2 \cdot 10^{-3}$ *M* Ca^{2+}	50–65[a]	15–25[a]
1 *M* NaOH + $2 \cdot 10^{-3}$ *M* Sr^{2+}	40–45[a]	11–20[a]
1 *M* NaOH + $2 \cdot 10^{-3}$ *M* Ba^{2+}	25–30[a]	6–15[a]

[a] Shows a range of values for 3 different Pt electrodes

find how much hydrogen peroxide was originally formed by the electrochemical process, the efficiencies measured for various electrolysis times were plotted against time as shown in Fig. 8. From the efficiency values obtained by extrapolation to zero time, one can see that oxygen is reduced to OOH^- with an efficiency of 100% in 1 *M* NaOH at an anodized platinum electrode. In other solutions an electrochemical process that produces hydrogen peroxide occurs to the extent of 15–60%, depending on the composition of the solutions. The efficiency values obtained by the extrapolation are shown in Table 3 for various concentrations of Br^- and alkaline-earth metal cations, in 1 *N* H_2SO_4 and 1 *M* NaOH, respectively.

The catalytic activity of anodized or cathodized platinum electrodes on hydrogen peroxide decomposition was actually measured as follows. Twenty-five ml of 1 *N* H_2SO_4 solution containing H_2O_2 at a concentration of 92 μg/ml was prepared with and without the addition of Br^- and put in the H-cell in the above experiments. A platinum electrode was dipped in the solution and oxygen gas was bubbled in order to stir the solution as in the efficiency measurements. One ml of the solution was taken out every 3 min and the hydrogen peroxide concentration was determined spectrophotometrically. The results are given in Fig. 9, and show that the H_2O_2 concentration decreases almost linearly with time except in the presence of KBr (10^{-4}–10^{-1} *M*). In a pure 1 *N* H_2SO_4 solution, the decomposition rate is much greater with a cathodized electrode than with an anodized electrode. Previous investigators also reported that platinum lost its catalytic activity for decomposing H_2O_2 in HCl solution[43,44,45]. We may conclude that the coulombic efficiency of less than 100% in 1 *N* H_2SO_4 containing Br^-, is not due to decomposition of hydrogen peroxide, but due to at least two electrochemical processes, one of which does not produce hydrogen peroxide electrochemically, or reduce H_2O_2 electrochemically by the reaction

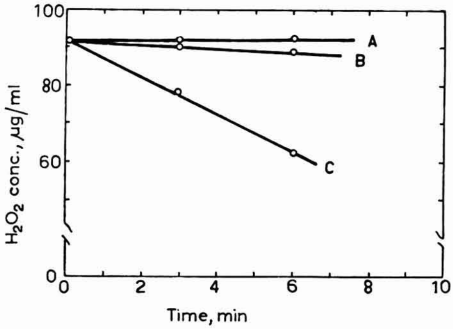


Fig. 9. H_2O_2 decomposition in 1 *N* H_2SO_4 with platinum electrodes. (A), represents six experiments with anodized or cathodized electrodes in 1 *N* H_2SO_4 containing KBr (10^{-4}, 10^{-3}, 10^{-1} *M*); (B), with an anodized electrode in 1 *N* H_2SO_4; (C), with a cathodized electrode in 1 *N* H_2SO_4.

$$H_2O_2 + 2\,H^+ + 2\,e = 2\,H_2O; \qquad E_{red}^\circ = 1.77.$$

An experiment similar to that of Fig. 9 was carried out in 1 *M* NaOH with and without the addition of Ba^{2+}. It was found that practically no hydrogen peroxide was decomposed without a platinum electrode in 1 *M* NaOH, and the decomposition rate was much greater with a cathodized electrode than that with an anodized electrode[21]. In the presence of Ba^{2+} ion the decomposition rate was greater by about 20% with either a cathodized or an anodized platinum electrode.

The method described above, by which electrochemical formation of H_2O_2 was found by extrapolating to zero-electrolysis time, has disadvantages. The determination of very small amounts of hydrogen peroxide formed in a short electrolysis time was not accurate; moreover, it was felt that the electrode surface was changing to some extent during the first one or two minutes in the constant current electrolysis, since the potential was changing.

In order to overcome these difficulties the following method was tried, using four differently treated platinum electrodes. Both the efficiencies (for 10 min of electrolysis at 1.0 mA) and the rates of hydrogen peroxide decomposition in a solution of 120 μg H_2O_2/ml were measured for the four electrodes in 1 M NaOH with or without the addition of Ba^{2+}. These results are plotted on a graph shown in Fig. 10. The four

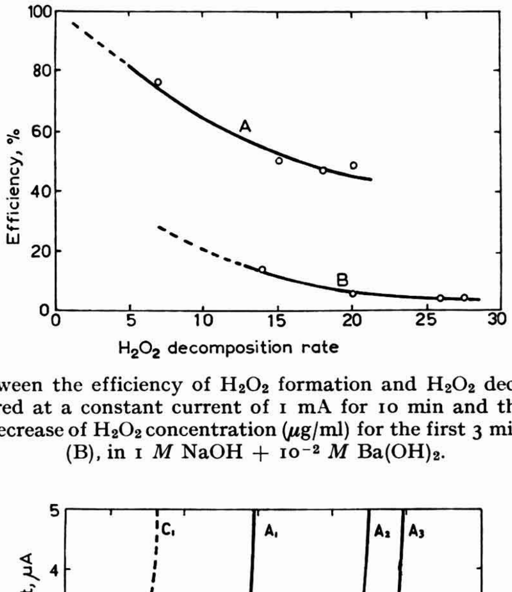


Fig. 10. Relation between the efficiency of H_2O_2 formation and H_2O_2 decomposition rate. The efficiency was measured at a constant current of 1 mA for 10 min and the decomposition rate was expressed in the decrease of H_2O_2 concentration (μg/ml) for the first 3 min. (A), in 1 M NaOH; (B), in 1 M NaOH + 10^{-2} M $Ba(OH)_2$.

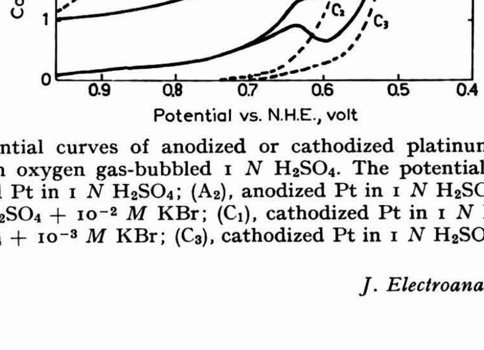


Fig. 11. Current–potential curves of anodized or cathodized platinum electrodes (apparent area 0.05 cm^2) taken in oxygen gas-bubbled 1 N H_2SO_4. The potential scanning rate was 1.2 mV/sec. (A_1), anodized Pt in 1 N H_2SO_4; (A_2), anodized Pt in 1 N H_2SO_4 + 10^{-3} M KBr; (A_3), anodized Pt in 1 N H_2SO_4 + 10^{-2} M KBr; (C_1), cathodized Pt in 1 N H_2SO_4; (C_2), cathodized Pt in 1 N H_2SO_4 + 10^{-3} M KBr; (C_3), cathodized Pt in 1 N H_2SO_4 + 10^{-2} M KBr.

points on each curve are for anodized, cathodized, *aqua regia*-treated, and heated (in air at 700°) platinum electrodes, respectively. The points taken in 1 *M* NaOH fall on one curve (A) and the points taken in [1 *M* NaOH + 10^{-2} *M* $Ba(OH)_2$] fall on the other curve (B). Extrapolation of curve A to zero decomposition rate goes to almost 100% efficiency and extrapolation of the curve B does not seem to go to zero. These results indicate that the electrode process of the oxygen reduction in 1 *M* NaOH with Ba^{2+} ion is different, at least to some extent, from that in pure 1 *M* NaOH, because if the low efficiency in the presence of Ba^{2+} is simply due to a higher rate of hydrogen peroxide decomposition both data should fall on curve A and the extrapolation to zero decomposition should go to 100% efficiency. We may conclude that oxygen is electrochemically reduced to OOH^- at platinum electrodes in 1 *M* NaOH, but in the presence of Ba^{2+} ion another electrochemical process takes place at the same time which does not produce hydrogen peroxide, or OOH^- is electrochemically reduced further.

(c) Current–potential curves. Current–potential curves of platinum electrodes were taken in 1 *N* H_2SO_4 and 1 *M* NaOH solutions under various conditions from positive to negative potentials. The results are shown in Figs. 11 and 12. The curves C_1 and A_1 in Fig. 11 show that the potential where the electrochemical oxygen reduction in a pure 1 *N* H_2SO_4 solution takes place with an appreciable rate, is about 140 mV more cathodic at an anodized electrode than at a cathodized electrode. This has already been found by voltammetry[14] and also by chronopotentiometry[7]. On addition of bromide ion to the solution, the current–potential curves shift to more cathodic potentials (curves A_2, A_3, C_2, C_3). This means overpotential for the oxygen reduction increases in the presence of bromide ion. Small peaks indicated by C″ with a small arrow on curves A_2 and A_3 are due to reduction of the oxide film ($PtO_2 \cdot n\,H_2O$) on the electrode surface. During the coulombic efficiency measurements in 1 *N* H_2SO_4 (Table 2) with an anodized platinum electrode (18 cm^2 surface area), the

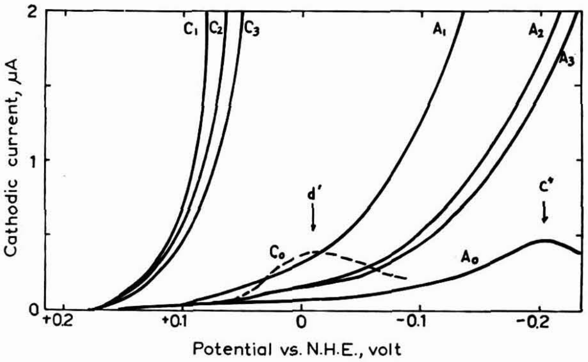


Fig. 12. Current–potential curves taken at anodized or cathodized platinum electrodes (apparent area, 0.05 cm^2) in 1 *M* NaOH. The potential scanning rate was 0.6 mV/sec. (A_0), anodized electrode in N_2-saturated 1 *M* NaOH; (A_1), anodized electrode in O_2-bubbled 1 *M* NaOH; (A_2), anodized electrode in O_2-bubbled 1 *M* NaOH + $4 \cdot 10^{-4}$ *M* $BaCl_2$; (A_3), anodized electrode in O_2-bubbled 1 *M* NaOH + $4 \cdot 10^{-3}$ *M* $BaCl_2$; (C_0), cathodized electrode in N_2-saturated 1 *M* NaOH; (C_1), cathodized electrode in O_2-bubbled 1 *M* NaOH; (C_2), cathodized electrode in O_2-bubbled 1 *M* NaOH + $4 \cdot 10^{-4}$ *M* $BaCl_2$; (C_3), cathodized electrode in O_2-bubbled 1 *M* NaOH + $4 \cdot 10^{-3}$ *M* $BaCl_2$.

electrode potential was measured and found that to change from 0.74 to 0.70 V *vs.* N.H.E. during electrolysis for 10 min in pure 1 *N* H_2SO_4, and from 0.50 to 0.37 V in (1 *N* H_2SO_4 + 10^{-2} *M* KBr). Comparing these potential values with the results of Fig. 11, one may conclude that in the coulombic efficiency measurements (Tables 2, 3) oxygen was being reduced on the PtO_2-covered surface at the anodized electrode in pure 1 *N* H_2SO_4 and also probably on the bromide-adsorbed surface which had no oxide film in the 1 *N* H_2SO_4 containing bromide.

In alkaline solution, again oxygen is reduced at more anodic potentials at a cathodized electrode than at an anodized electrode as shown by the curves C_1 and A_1 in Fig. 12. The overpotential for the oxygen reduction increases when Ba^{2+} is added, at both anodized and cathodized platinum electrodes. The peaks (d′) and (c″) correspond to reduction on the electrode surface of $Pt(OH)_2$ (or adsorbed oxygen) film, and $PtO_2 \cdot n\ H_2O$, respectively. The electrode potentials during the coulombic efficiency measurement in 1 *M* NaOH (Table 1) were −0.035 and +0.063 V *vs.* N.H.E. in pure 1 *M* NaOH for the anodized and the cathodized electrodes respectively, and −0.015 and +0.065 *vs.* N.H.E. in (1 *M* NaOH + $5 \cdot 10^{-3}$ *M* Ba^{2+}) for the anodized and the cathodized electrodes, respectively. Comparing these potentials with the reduction of the oxide films [peak (d′) and (c″)], one can conclude that in the coulombic efficiency measurements oxygen was being reduced on the PtO_2-covered surface at the anodized electrode and on the $Pt(OH)_2$-covered (at least in parts) surface at the cathodized electrode in 1 *M* NaOH regardless of the presence or absence of Ba^{2+} ion.

(d) Influence of pH, current density and potential. The current efficiency for the hydrogen peroxide production in a neutral solution (pH 7.0) was measured at an anodized electrode. The results are shown in Table 4, which shows that the efficiency values (No. 1, 2, and 3 in Table 4) fall between the efficiency values in 1 *M* NaOH and 1 *N* H_2SO_4 solutions (Tables 1 and 2). Addition of bromide increases the efficiency, and addition of zinc ion decreases it a little, as would be expected from the results obtained above on the addition of anions and cations in alkaline and acid solutions.

TABLE 4

CURRENT EFFICIENCY FOR H_2O_2 FORMATION IN A NEUTRAL SOLUTION AT AN ANODIZED PLATINUM ELECTRODE

No.	*Electrolyte*	*Electrolysis time (min)*	*H_2O_2 formed*[a] *(μg)*	*Efficiency (%)*
1	0.2 *M* NaAc + HAc (pH 7.0)	5	11.6	18.4
2	0.2 *M* NaAc + HAc (pH 7.0)	10	18.7	17.6
3	0.2 *M* NaAc + HAc (pH 7.0)	15	28.0	17.6
4	0.2 *M* NaAc + HAc + 0.03 *M* KBr	10	46.7	44.0
5	0.2 *M* NaAc + HAc + 0.1 *M* KBr	10	45.5	43.0
6	Solution of No. 4 + 0.01 *M* $ZnSO_4$	10	38.0	35.9
7	Solution of No. 4 + 0.05 *M* $ZnSO_4$	10	38.5	36.3

[a] At an anodized electrode 18 cm^2 in area at a constant current of 1.0 mA.

The efficiency for the hydrogen peroxide formation was also measured over a wide potential range in 1 *M* NaOH. The results are shown in Fig. 13, the measurements for which were carried out by passing a current of 1–18 mA/electrode 16 cm^2 in area for 2.5–15 min depending on the current. It can be seen from the figure, that the efficiency values decrease with decrease in electrode potential. The factors contributing to this would be as follows. First, in a cathodic potential range, the platinum surface is no longer covered with oxide film, but to some extent with adsorbed hydrogen and the catalytic activity for decomposing hydrogen peroxide may be greater than those at anodic potentials where an oxide film exists on the surface. Decomposition of hydrogen peroxide on platinum has been considered as an electrochemical process[46,47] and therefore should be dependent on the electrode potential. Secondly, at the most cathodic potential (—0.775 V), 18 mA/16 cm^2 had to be passed in order to maintain the potential and this may be a little over the diffusion-limiting current. The diffusion-limiting current calculated (from $i_l = nFDC/\delta$) was 1.0 mA/cm^2, making the following assumptions: $\delta = 0.005$ cm for the gas-stirred solution, $C = 0.8 \times 10^{-6}$ mole/cm^3, $n = 2$, and $D = 2.7 \times 10^{-5}$ cm^2 sec^{-1}. Thirdly, some other oxygen reduction processes and a hydrogen peroxide reduction process (*e.g.*, $OOH^- + H_2O + 3\,e \rightarrow 3\,OH^-$) are taking place to a greater extent at the cathodic potential than at the anodic potential.

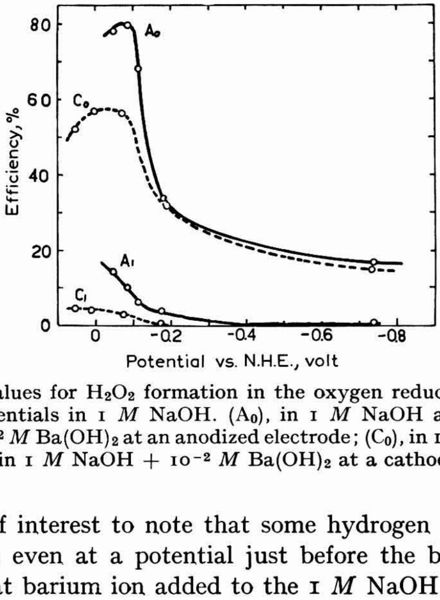


Fig. 13. The efficiency values for H_2O_2 formation in the oxygen reduction process at platinum electrodes at various potentials in 1 *M* NaOH. (A_0), in 1 *M* NaOH at an anodized electrode; (A_1), in 1 *M* NaOH + 10^{-2} *M* $Ba(OH)_2$ at an anodized electrode; (C_0), in 1 *M* NaOH at a cathodized electrode; (C_1), in 1 *M* NaOH + 10^{-2} *M* $Ba(OH)_2$ at a cathodized electrode.

At any rate, it is of interest to note that some hydrogen peroxide formation is certainly taking place even at a potential just before the beginning of hydrogen evolution and also that barium ion added to the 1 *M* NaOH still has the effect of decreasing the H_2O_2 formation, although the electrode surface is not covered with oxide film at this cathodic potential. Further work is necessary to make this point clear.

3. Effects of cations and anions on oxygen evolution

(a) Platinum electrodes. Current–potential curves for the oxygen-evolution process were taken at a platinum electrode in 1 *M* NaOH from +0.6 V toward the more anodic direction. The effect of the addition $NaClO_4$, $Sr(ClO_4)_2$ and EDTA to the solution are shown in Fig. 14. The results show that the electrode surface seems to attain a constant state after the first two successive curves (curves 1, 2, 3), and the addition of 10^{-2} *M* $NaClO_4$ (and also KCl in a separate experiment) has very little

effect (curves 3, 4). The overpotential for the oxygen-evolution process increases with increasing additions of $Sr(ClO_4)_2$ (curve 5, 6, 7) and the addition of EDTA brings the curve back to the original position, probably because Sr^{2+} ions are complexed and no Sr^{2+} can be adsorbed on the surface.

The increase in the overpotential for the three alkaline-earth ions at the same concentration was in the following order: $Ca^{2+} > Sr^{2+} > Ba^{2+}$. However, the solubility of $Ca(OH)_2$ in 1 *M* NaOH is so small that the effect of Ca^{2+} could not be properly evaluated.

There is some doubt concerning the function of EDTA in the experiment described above; it is possible that EDTA may be electrochemically oxidized on the platinum electrode in 1 *M* NaOH, in addition to forming a complex with Sr^{2+} ion. In order

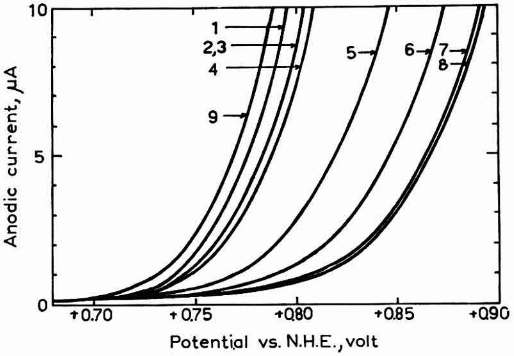


Fig. 14. Current–potential curves of an anodized platinum electrode (0.13 cm^2 in surface area for the oxygen-evolution process in an O_2 gas-bubbled 1 *M* NaOH solution. The potential scanning rate was 0.6 mV/sec. These curves were taken in the following order: (1), 1st run in 1 *M* NaOH; (2), 2nd run immediately after the 1st run in 1 *M* NaOH; (3), 3rd run immediately after the 2nd run in 1 *M* NaOH; (4), in 1 *M* NaOH + 10^{-2} *M* $NaClO_4$ after curve (3); (5), in 1 *M* NaOH + 10^{-2} *M* $NaClO_4$ + 10^{-4} *M* $Sr(ClO_4)_2$ after curve (4); (6), in 1 *M* NaOH + 10^{-2} *M* $NaClO_4$ + 10^{-3} *M* $Sr(ClO_4)_2$ after curve (5); (7), in 1 *M* NaOH + 10^{-2} *M* $NaClO_4$ + 10^{-2} *M* $Sr(ClO_4)_2$ after curve (6); (8), repeated in the same condition as curve (7); (9), in 1 *M* NaOH + 10^{-2} *M* $NaClO_4$ + 10^{-2} *M* $Sr(ClO_4)_2$ + $2 \cdot 10^{-2}$ *M* EDTA.

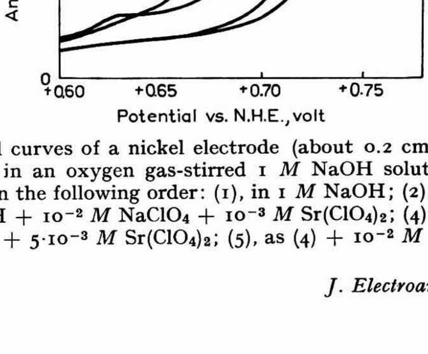


Fig. 15. Current–potential curves of a nickel electrode (about 0.2 cm^2 in surface area) for the oxygen-evolution process in an oxygen gas-stirred 1 *M* NaOH solution taken at 0.6 mV/sec. These curves were taken in the following order: (1), in 1 *M* NaOH; (2), in 1 *M* NaOH + 10^{-2} *M* $NaClO_4$; (3), in 1 *M* NaOH + 10^{-2} *M* $NaClO_4$ + 10^{-3} *M* $Sr(ClO_4)_2$; (4), in 1 *M* NaOH + 10^{-2} *M* $NaClO_4$ + $5 \cdot 10^{-3}$ *M* $Sr(ClO_4)_2$; (5), as (4) + 10^{-2} *M* EDTA.

to examine this possibility, 25 ml of (1 *M* NaOH + 0.020 *M* EDTA) solution was electrolyzed in an H-cell with a platinum electrode (6.0 cm^2) as anode at a current density of 1.0 mA/cm^2 up to 60 min under oxygen gas stirring. The concentration of the EDTA was determined every 20 min by titrating a 5.0-ml portion of the solution with a standard solution of 0.0100 *M* $ZnSO_4$ using Eriochrome Black T as indicator. During the electrolysis the electrode potential rose from an initial value of +0.865 to +1.055 V *vs.* N.H.E. at the end of the electrolysis. It was found that the concentration of the EDTA solution remained constant within analytical error even after 60 min. This suggests that EDTA is not oxidized electrochemically under these conditions.

(b) Other electrodes. The same experiments as for the platinum electrode were carried out to confirm the effect of Ba^{2+}, Sr^{2+}, and Ca^{2+} in 1 *M* NaOH for nickel, palladium, nickel oxide, gold, and graphite electrodes. The results for a nickel electrode are shown in Fig. 15; the relative effect of Sr^{2+} and EDTA are essentially the same as for a platinum electrode except that oxygen evolution takes place at much lower potentials on nickel than on platinum. Tafel slopes were obtained from these current–potential relations. These results are summarized in Table 5, which shows that the oxygen overpotential increases by 15–90 mV in the presence of $5 \cdot 10^{-3}$ *M* $Sr(ClO_4)_2$ depending on the electrode material, and the Tafel slope increases only slightly in most cases when $Sr(ClO_4)_2$ is added in 1 *M* NaOH.

TABLE 5

INFLUENCE OF Sr^{2+} ON THE OXYGEN OVERPOTENTIAL

Electrode	*Potential at 0.05 mA/cm² (vs. N.H.E.)*		*Potential increase (mV)*	*Tafel slopes (mV/decade)*	
	1 M NaOH (V)	*1 M NaOH + $5 \cdot 10^{-2}$ M $Sr(ClO_4)_2$*		*1 M NaOH*	*1 M NaOH + $5 \cdot 10^{-3}$ M $Sr(ClO_4)_2$*
Ni	0.678	0.738	60	72	85
Pd	0.754	0.769	15	85	85
Pt	0.785	0.875	90	57	80
NiO[a]	0.823	0.901	78	54	77
Au	0.858	0.928	70	67	77
Graphite[b]	0.935	0.978	43	105	105

[a] Prepared by heating a nickel rod at 700° for 10 min.

[b] A graphite rod for the spectrographic analysis.

4. DISCUSSION

In order to understand the considerable effect of small amounts of anions and cations added to the electrolyte as described in the preceding sections, we must assume that these ions are adsorbed on the electrode surface. First the nature of the adsorption mechanism has to be discussed.

Various metal oxides with hydrated surfaces generally have an ion-exchange property. The hydroxyl groups which exist on the surface of these metal oxides in aqueous solutions usually dissociate in two ways depending on the pH of the solution[9], that is

$$\vdots\mathrm{M{-}OH} \rightleftharpoons \vdots\mathrm{M}^{+} + \mathrm{OH}^{-} \text{ (in acid solutions)} \tag{5}$$

$$\vdots\mathrm{M{-}OH} \rightleftharpoons \vdots\mathrm{MO}^{-} + \mathrm{H}^{+} \text{ (in alkaline solutions)} \tag{6}$$

where $\vert M$ represents a metal atom on the surface of the oxide. These OH^- or H^+ ions are held near the $\vert M^+$ or $\vert MO^-$, respectively. Therefore, anion exchange-adsorptions in acid solutions and cation exchange-adsorptions in alkaline solutions take place as shown in the eqns. (7) and (8) respectively:

$$\vert M^+OH^- + Cl^- \rightarrow \vert M^+Cl^- + OH^- \qquad (7)$$

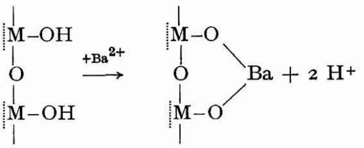
$$\vert MO^-H^+ + M^+ \rightarrow \vert MO^-M^+ + H^+ \qquad (8)$$

The platinum electrode is covered with oxide film in a certain potential range; therefore, anion adsorption in acid solution and cation adsorption in alkaline solution should be expected on the electrode surface.

It has been shown that O_2 is reduced on a PtO_2-covered surface at an anodized electrode and on a surface covered with $Pt(OH)_2$ (or adsorbed oxygen) at a cathodized electrode in 1 *M* NaOH (Fig. 12), and that a small amount of Ba^{2+}, Sr^{2+}, and Ca^{2+} had a considerable effect (Table 1). These cation effects can be explained on the basis of ion-exchange adsorption.

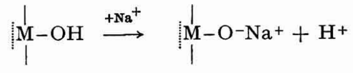
The anion effect on oxygen reduction found in acid solution, (Table 2), can be explained on the basis of anion exchange adsorption; however, the electrode surface is no longer covered with oxide film in the presence of Br^- ion during the oxygen reduction (Fig. 11). This anion effect in acid and neutral solutions, therefore, can only be a result of the specific adsorption of halide ions. The influences of such specific adsorption of halide ions on various electrode processes has frequently been described in the literature[48,49,50].

It has previously been suggested[10,11] that the nature of the divalent cation adsorption on metal oxides is not due to a simple electrostatic attraction, as in an ordinary organic ion-exchanger, but to a kind of co-ordination bonding; a surface complex mechanism involving a six-membered ring with the surface atoms, which is much more stable than the ionic bonding, has been proposed. According to this mechanism the surface hydroxyl groups make a surface complex with Ba^{2+} ion, for example, as follows:



(9)

If the adsorption force were an ordinary electrostatic attraction, Na^+ would be adsorbed rather than Ba^{2+} in 1 *M* NaOH, as follows:



$$\vert M{-}OH \xrightarrow{+Na^+} \vert M{-}O^-Na^+ + H^+ \qquad (10)$$

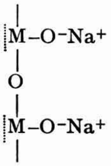
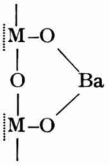
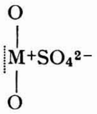
because the concentration of Na^+ is far greater than that of Ba^{2+} and total molarity of the electrolyte is high in the experimental conditions of this paper[51].

It was shown that Ba^{2+}, Sr^{2+}, and Ca^{2+} ions had a marked effect on the oxygen-evolution process. This means these positively charged ions must have been adsorbed on the platinum electrode at such a positive potential. This also indicates that electrostatic attraction between the divalent cation and the electrode surface is not the adsorption force, but the surface complex formation described above is probably involved.

One can summarize (see Table 6) a relation between the surface condition of the platinum electrode and the main process for oxygen reduction. At the first Surface, Na^+ ions may be held by an electrostatic attraction around the negatively-charged surface and in Surface 3, SO_4^{2-} ion may be held near the surface in the same way. Surface 4 shows the specific adsorption of Br^-. Although the main electrochemical reaction for oxygen reduction was found to be dependent on the surface state of the platinum electrode, such as adsorption on the surface as well as on the electrode potential, the detailed mechanism of these electrode processes will have to be elucidated by further research.

TABLE 6

MAIN OXYGEN REDUCTION REACTION AT AN ANODIZED Pt ELECTRODE WITH VARIOUS ELECTROLYTES

Electrolyte	*Electrode surface*[a]	*Main reaction*	*Proportion*[b] *(%)*	*Potential*[c] *vs. N.H.E.*
1 *M* NaOH	(Surface 1)  $\mathrm{M{-}O^{-}Na^{+}}$ O $\mathrm{M{-}O^{-}Na^{+}}$	$O_2 \rightarrow OOH^-$	80–100	−0.035
1 *M* NaOH + 10^{-3} *M* Ba^{2+}	(Surface 2)  $\mathrm{M{-}O}$ O Ba $\mathrm{M{-}O}$	$O_2 \rightarrow OH^-$	69–80	−0.055
1 *N* H_2SO_4	(Surface 3)  O $\mathrm{M^{+}SO_4^{2-}}$ O	$O_2 \rightarrow H_2O$	90–100	+0.737
1 *N* H_2SO_4 + 10^{-2} *M* Br^-	(Surface 4)  O $\mathrm{M{-}Br}$ O	$O_2 \rightarrow H_2O_2$	50–65	+0.497

[a] ⁝M represents the metallic atom in the metal oxide films on the electrode surface.
[b] Proportion of the main oxygen reduction reaction to the total current.
[c] Potential during the constant current electrolysis at 1.0 mA/16 cm^2.

ACKNOWLEDGEMENTS

The author wishes to thank Professor E. YEAGER, Western Reserve University, and Professor W. C. VOSBURGH, Duke University, for their valuable suggestions in the preparation of this paper. This work has been partly supported by the U. S. Office of Naval Research, Contract Nonr 2391(00).

SUMMARY

The effects of the addition 10^{-4}–10^{-1} *M* of various anions and cations to 1 *N* H_2SO_4 or 1 *M* NaOH solutions on oxygen-reduction at pre-anodized and pre-cathodized platinum electrodes were examined by measuring coulombic efficiency for formation of hydrogen peroxide (calculated on the basis of $O_2 + H_2O + 2e \rightarrow OOH^- + OH^-$) and also by current–potential curves. In 1 *M* NaOH, oxygen was reduced to hydrogen peroxide with an efficiency of almost 100% at the pre-anodized electrode. However, in the presence of Ba^{2+}, Sr^{2+}, and Ca^{2+} in 1 *M* NaOH, the efficiency decreased to 10–15% with increasing concentration of the ions. In 1 *N* H_2SO_4, oxygen was reduced mainly to water and the coulombic efficiency for hydrogen peroxide formation was only 10–20%, but in the presence of Cl^- and Br^- ions this efficiency increased to 50–60%. Current–potential curves indicated that overpotential of the oxygen reduction at the platinum electrodes increased in the presence of Ba^{2+}, Sr^{2+}, and Ca^{2+} ions in 1 *M* NaOH, and in the presence of Cl^- and Br^- ions in 1 *N* H_2SO_4. Catalytic activity of the platinum electrodes for hydrogen peroxide decomposition in 1 *M* NaOH and 1 *N* H_2SO_4 with and without the addition of the anions and cations was also measured.

These results are discussed on the basis of ion-exchange adsorption of cations and anions on the oxide-covered platinum electrodes. It is concluded that the oxygen reduction on platinum is not one process, but at least two processes including $O_2 + H_2O + 2e \rightarrow OOH^- + OH^-$ in alkaline solution and $O_2 + 2H^+ + 2e \rightarrow H_2O_2$ in acid solution, and the proportion of hydrogen peroxide formation depends on the surface condition of the electrode, such as presence of oxide film and/or adsorption of anions and cations.

Oxide films and/or adsorbed oxygen which exist on the platinum electrodes were summarized and a voltammetric study of a special oxide film formed on an excessively anodized platinum electrode was described. Overpotential of oxygen evolution on other metals and graphite as well as on Pt in 1 *M* NaOH increased by 15~90 mV when Ba^{2+}, Sr^{2+}, or Ca^{2+} ions were added to the electrolyte.

REFERENCES

1 S. Wakkad and S. H. Emara, *J. Chem. Soc.*, (1952) 461.
2 M. Breiter, *Electrochim. Acta*, 5 (1961) 145.
3 A. Kozawa, *J. Electrochem. Soc. Japan*, 31 (1963) 315.
4 S. W. Feldberg, C. G. Enke and C. E. Bricker, *J. Electrochem. Soc.*, 110 (1963) 826.
5 F. C. Anson and J. J. Lingane, *J. Am. Chem. Soc.*, 79 (1957) 4901.
6 F. C. Anson, *J. Am. Chem. Soc.*, 81 (1959) 1554.
7 J. J. Lingane, *J. Electroanal. Chem.*, 2 (1961) 296.
8 M. Breiter, *J. Electrochem. Soc.*, 109 (1962) 622, 1099.
9 C. B. Amphlett, L. A. Donald and M. J. Redman, *J. Inorg. & Nucl. Chem.*, 6 (1958) 236.
10 A. Kozawa, *J. Electrochem. Soc.*, 106 (1959) 552.
11 A. Kozawa, *J. Inorg. & Nucl. Chem.*, 21 (1961) 315.
12 H. A. Laitinen and I. M. Kolthoff, *J. Phys. Chem.*, 45 (1941) 1061.
13 D. T. Sawyer and L. V. Interrante, *J. Electroanal. Chem.*, 2 (1961) 310.
14 A. Kozawa, *J. Electrochem. Soc. Japan*, 31 (1963) 183.
15 J. J. Lingane, *J. Electroanal. Chem.*, 2 (1961) 296.
16 J. O'M. Bockris and A. K. M. S. Huq, *Proc. Roy. Soc. London, Ser. A*, 237 (1956) 277.
17 W. Berl, *Trans. Electrochem. Soc.*, 83 (1943) 253.
18 M. Davis, M. Clark, E. Yeager and F. Hovorka, *J. Electrochem. Soc.*, 106 (1959) 56.
19 H. A. Laitinen and I. M. Kolthoff, *J. Phys. Chem.*, 45 (1941) 1061.
20 P. Delahay, *J. Electrochem. Soc.*, 97 (1950) 198, 205.

21 A. Kozawa, *J. Electrochem. Soc. Japan*, 31 (1963) 719.
22 A. Kozawa, *J. Electrochem. Soc. Japan*, 31 (1963) 682.
23 M. Breiter, *Advances in Electrochemistry and Electrochemical Engineering*, Vol. 1, edited by P. Delahay, Interscience Publishers, New York, 1961 p. 123.
24 M. A. Gerovich, R. I. Kaganovich, V. A. Vergelesov and L. N. Gorokhov, *Dokl. Akad. Nauk SSSR*, 114 (1957) 1049.
25 R. I. Kaganovich, M. A. Gerovich and E. Kh. Enikeev, *Dokl. Akad. Nauk SSSR*, 108 (1956) 107.
26 A. Hickling and S. Hill, *Trans. Faraday Soc.*, 46 (1950) 550.
27 T. Erdey-Grúz and I. Shafarik, *Soviet Electrochemistry, Proceedings of the 4th Conference of Electrochemistry*, Vol. 2, Consultant Bureau, New York, 1961, p. 145.
28 W. C. Wolfe, *Anal. Chem.*, 34 (1962) 1328.
29 A. Kozawa, *J. Electrochem. Soc. Japan*, 30 (1962) 720.
30 J. A. V. Butler and G. Armstrong, *Proc. Roy. Soc. London, Ser. A*, 137 (1932) 604.
31 J. D. Pearson and J. A. V. Butler, *Trans. Faraday Soc.*, 34 (1938) 1163.
32 A. Hickling, *Trans. Faraday Soc.*, 41 (1945) 333.
33 F. Will and C. A. Knorr, *Z. Elektrochem.*, 64 (1960) 258.
34 W. Bold and M. Breiter, *Z. Elektrochem.*, 64 (1960) 897.
35 T. C. Frankline and S. L. Cooke, *J. Electrochem. Soc.*, 107 (1960) 557.
36 K. Nagel and H. Dietz, *Electrochim. Acta*, 4 (1961) 141.
37 K. Nagel and H. Dietz, *Electrochim. Acta*, 4 (1961) 1.
38 T. Inoue, *J. Electrochem. Soc. Japan*, 25 (1957) 381, 418, 576.
39 R. Ruer, *Z. Physik. Chem. Leipzig*, 44 (1903) 81.
40 S. Altmann and R. H. Busch, *Trans. Faraday Soc.*, 45 (1949) 720.
41 S. Shibata, *Bull. Chem. Soc. Japan*, 36 (1963) 525.
42 H. Boer, *Rec. Trav. Chim.*, 67 (1948) 217; 70 (1951) 1020.
43 G. Bianchi, F. Mazza and T. Mussini, *Electrochim. Acta*, 7 (1962) 457.
44 M. A. Heath and J. H. Walton, *J. Phys. Chem.*, 37 (1933) 977.
45 S. W. Pennycuick, *J. Am. Chem. Soc.*, 52 (1930) 4621; 61 (1939) 2234.
46 J. Weiss, *Trans. Faraday Soc.*, 31 (1935) 1547.
47 H. Gerischer, *Z. Physik. Chem. Frankfurt*, 6 (1956) 178.
48 B. Breyer, F. Gutmann and S. Hacobian, *Australian J. Sci. Research, Ser. A*, 4 (1951) 595.
49 A. Kozawa, S. Mase and T. Takahashi, *J. Metal Finishing Soc. Japan*, 12 (1961) 303.
50 P. V. Popat and N. Hackerman, *J. Phys. Chem.*, 62 (1958) 1198.
51 F. Helfferich, *Ion Exchange*, McGraw-Hill, New York, 1962, p. 157.
52 I. Yablokova and V. Bagotsky, *Dokl. Akad. Nauk USSR*, 85 (1952) 599.
53 E. Yeager, P. Krouse and K. Rao, *Kinetics of the Oxygen–Peroxide Couple on Carbon*, CITCE Meeting, Moscow, August 1963; Technical Report 16, Western Reserve University, U.S. Office of Naval Research, Contract Nonr 2391(00), June 1963.
54 E. Yeager and A. Kozawa, *Kinetic Factors in Fuel Cell Systems, The Oxygen Electrode*, Technical Report 17, Western Reserve University, U.S. Office of Naval Research, Contract Nonr 2391(00), January 1964.

DERIVATIVE POLAROGRAPHIC TITRATION OF TERTIARY AMINES AND SALTS OF ORGANIC ACIDS IN ACETIC ACID IN THE PRESENCE OF ANTIMONY AND QUINHYDRONE ELECTRODES

VILIM VAJGAND AND TIBOR PASTOR

Faculty of Sciences, Institute of Chemistry, Belgrade (Yugoslavia)

(Received September 13th, 1963)

Derivative polarographic titration, originating from REILLEY, COOKE AND FURMAN[1], has only recently been applied for the determination of some substances in non-aqueous solutions. SHAIN AND SVOBODA[2] have titrated weak organic acids with tetrabutylammonium hydroxide using acetone as solvent in the presence of two polarized Pt micro-electrodes and have observed that the titration end-point coincided with the maximum potential difference obtained in the course of the titration. Such a maximum was more marked than the change of potential in classical potentiometry. The effect of the polarization of electrodes on the potential jump was studied by ROSS AND SHAIN[3] as well as by HARLOW, NOBLE AND WYLD[4]. The latter authors, titrating potentiometrically weak acids in ethylenediamine in the presence of a polarized Pt-electrode, have obtained potential jumps two to three times as great as those obtained with glass electrodes. SVOBODA[5] has determined amines in a mixture of *m*-cresol and acetonitrile by a derivative polarographic method. However, when attempting the determination of the same amines in glacial acetic acid, which is the most common solvent used in non-aqueous titrations, he neither obtained reproducible results nor a sharp maximum at the titration end-point.

A platinum electrode is unsuitable for the measurement of the acidity of a solution since it is not fully reversible; its potential is dependent upon time and the results are not reproducible. We have assumed that the addition of quinhydrone, which reacts reversibly in acid media, would eliminate this disadvantage of the Pt-electrode in glacial acetic acid. A similar effect can be expected from the use of other reversible reacting electrodes (antimony, hydrogen etc.).

Derivative polarographic titrations have so far not been performed in the presence of quinhydrone electrodes. Antimony electrodes have mostly been applied for titrations in aqueous solutions. ENOKI AND MIRISAKA[6] have used antimony electrodes in derivative polarographic titrations of acids and bases in aqueous and alcoholic solutions. BISHOP AND SHORT[7,8,9] have used antimony electrodes in aqueous solutions and made detailed studies of electrode processes, examining various factors which alter the potential during titration.

We have used antimony and quinhydrone electrodes in derivative polarographic titrations with perchloric acid of tertiary amines and salts of organic acids in a mixture of glacial acetic acid and acetic acid anhydride. The properties of antimony and quinhydrone electrodes as well as the results obtained in their presence are presented in this work.

EXPERIMENTAL

Our experiments were performed with the apparatus shown in Fig. 1. The current source was a 2-V lead storage battery. Titrations in the presence of quinhydrone were performed with electrodes of Pt-wire, 1.2 cm long, and 0.5 mm in diameter, which were sealed into glass rods so that their distance apart (2 cm) remained constant during the titration. We have also used Pt-electrodes of 1 cm^2 surface area, the distance between which could be arbitrarily changed. Tungsten electrodes, 1-cm long, and 3 mm in diameter were also used. For titrations in the presence of antimony electrodes, two Radiometer electrodes were used. A resistance box from 1 kΩ–11 MΩ was used for the adjustment of the necessary current strength. The potential difference between electrodes was measured by means of a Radiometer 22 p pH-meter. For the potentiometric determination of the substances under investigation, a glass electrode and a mercury–mercurous acetate ($Hg/Hg_2(CH_3COO)_2$) electrode containing a saturated solution of sodium perchlorate in glacial acetic acid[10] was used; for derivative polarographic titration in the presence of quinhydrone the solution was saturated with quinhydrone (Analar) prior to the titration.

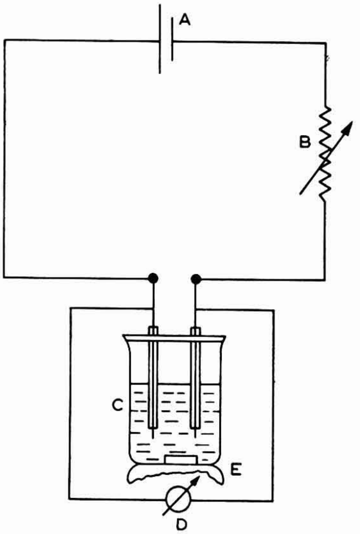


Fig. 1. A, storage battery; B, decade resistance box; C, cell with electrodes; D, pH-meter, E magnetic stirrer.

The solvent used was glacial acetic acid (Merck or Fluka p.a.), in a mixture with acetic acid anhydride (Carlo Erba or Kemika p.a.). 0.1 *N* perchloric acid solution was standardized with a solution of either sodium acetate or potassium hydrogen phthalate in glacial acetic acid. A standard solution of sodium acetate was prepared from the appropriate amount of sodium carbonate (Merck p.a.), previously dried at 270°.

In titrations of hydrochlorides of organic bases a 3% mercuric acetate solution was added to the solvent mixture.

Titrations of liquid amines (triethyl-, triheptyl-amine etc.) were carried out by taking a measured volume of the aqueous solutions of the amine prepared by weighing a definite amount in a volumetric flask and diluting to the desired volume.

Preliminary investigations have shown that either the application of reversible electrodes or the presence of a reversible system in the solution can solve the problem of derivative polarographic titration in glacial acetic acid. The addition of quinhydrone to the solution in the presence of platinum or tungsten electrodes or the use of antimony electrodes fulfilled the above requirement.

Behaviour of quinhydrone electrodes

Detailed investigations have shown that in the presence of quinhydrone a sharp maximum was obtained at the end-point of the titration, the results of the analysis being fully reproducible. The rate of potential establishment depends upon the titrated substance. The common feature of all systems investigated so far, is that the potential is more rapidly established before the titration end-point, than at the equivalence point and after. In order to determine which electrode process is characteristic for a titration, we have measured, in the course of titration, the changes of potential, at both the anode and the cathode with respect to a fibre-type saturated calomel electrode (S.C.E.), (Fig. 2). We have observed that the anode potential is slowly attained in the vicinity of the equivalence point and after it. In the course of the titration the potential increases constantly; in most of the titrated systems an enhanced potential jump appeared at the titration end-point. On the other hand, the potential at the cathode is rapidly attained; it is also constantly increasing, *i.e.*, is becoming more positive. An abrupt change of the potential also appears at the cathode, in dependence of the titrated system. It is important to note that the

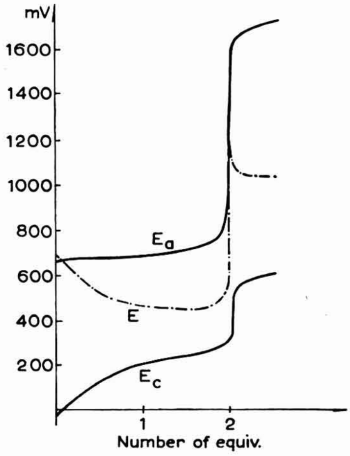


Fig. 2. Changes of anodic potential (E_a), cathodic potential (E_c), and their difference (E), during the titration of a $3 \cdot 10^{-2}$ *M* solution of antipyrine in the presence of quinhydrone electrodes.

potential rise on the cathode is smaller than that on the anode. Accordingly, it is obvious, that the shape of the titration curve (depicted in Fig. 2) depends upon the electrode processes at both the anode and the cathode, whereas the rate of attainment of the potential difference depends only upon the process at the anode.

Our investigations have shown that the concentration of acetic anhydride effects the magnitude of the potential change at the titration end-point. The maxima obtained are more enhanced in the presence of an excess of acetic anhydride, and the potential jump at the anode is from 300–400 mV per 0.01 ml of 0.1 *N* perchloric acid solution. We have therefore determined water content of glacial acetic acid by the Karl Fischer method[11], and have then added sufficient acetic acid anhydride so that the ratio acetic acid: acetic anhydride is 5 : 1. However, when titrating some substances, for instance, caffeine and caffeine–sodium benzoate, an excess of acetic anhydride was necessary.

The sharpness of the titration end-point is also affected by the size of the platinum electrode surface. An increase of surface results in a decrease in the maximum height. However, no significant differences in maximum height were observed using electrodes of 0.19 and 1 cm^2.

The amount of quinhydrone used affects neither the accuracy of the results nor the shape of the titration curves but the maxima obtained in the absence of quinhydrone are significantly smaller thus rendering the estimation of the titration end-point more difficult; in addition, the results obtained are not in good agreement.

Behaviour of antimony electrodes

Antimony electrodes were found to be very convenient for titrations ot tertiary amines and alkali salts of organic acids. The height of the maximum depended upon

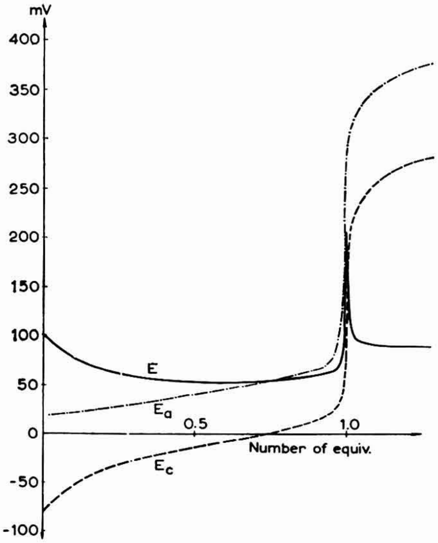


Fig. 3. Changes of anodic potential (E_a), cathodic potential (E_c), and their difference (E), during the titration of a $3 \cdot 10^{-2}$ *M* solution of sodium benzoate in the presence of two antimony electrodes.

the strength of the titrated base, *e.g.*, in the titration of diethylaniline ($K = 4.5 \times 10^{-8}$, in water) dissolved in a mixture of glacial acetic and acetic anhydride (1 : 1), a change in potential difference of about 140 mV per 0.1 ml of added perchloric acid solution was obtained at the equivalence point. However, the change for caffeine ($K = 4.1 \times 10^{-14}$ in water), under the same experimental conditions, amounted only to about 15 mV per 0.1 ml of titrant. The sharpness of the titration end-point, as with the quinhydrone electrode, depended also upon the composition of the solvent, *e.g.*, the change of potential difference at the equivalence point of brucine dissolved in a mixture of acetic acid and acetic anhydride (6 : 1) was 50 mV per 0.1 ml of 0.1 *N* perchloric acid solution but was 120 mV when the solvent consisted of equal parts (1 : 1) of acid and anhydride. Similar results were obtained with other titrating systems.

By measuring the anode and cathode potential against a S.C.E. during titration, we obtained curves of bilogarithmic shape as with titrations carried out in the presence of quinhydrone (Fig. 3). The titration end-point, determined by measuring the changes of the anodic potential, is observed slightly before the equivalence point, but when determined from cathodic potential changes, it occurs slightly after the equivalence point. The deviations obtained are 0.02–0.03 ml of 0.1 *N* perchloric acid solution. The same effect, although to a much less extent was observed also in the presence of quinhydrone electrodes. This phenomenon might be ascribed to the effect of concentration polarization, caused by constant current flow; therefore, the concentration of hydrogen ions at the anode is increased and that at the cathode is decreased. The curve obtained in derivative polarographic titration depicts the difference between the anodic and the cathodic potentials in the course of titration; its maximal value denotes the equivalence point.

Titration procedures and results

For each derivative polarographic titration in glacial acetic acid, 0.1–0.2 g of the substance to be titrated was weighed (taking into account the amounts taken in procedures given in pharmacopoeias). The determinations were carried out using pharmaceutical products, the purity of which were checked by potentiometric titration. The concentrations of the titrated solutions ranged from 0.03–0.05 *M*. Preliminary investigations indicated the possibility of titrating more diluted solutions. Satisfactory results were obtained for the titration of 0.01 *M* sodium hydrogen phthalate with 0.01 *M* perchloric acid solution.

The substances investigated behaved very differently when titrated, (Fig. 4). Sodium acetate, potassium hydrogen phthalate, sodium *p*-aminosalicylate, sodium benzoate, procaine HCl, caffeine, 1-phenyl-3-methyl-pyrazolone-5, isoniazide and antipyrine gave only one maximum corresponding to one equivalent of perchloric acid, whereas aminopyrine gave two maxima, the first of which was sharp and corresponded to one equivalent of perchloric acid. The other, although higher, could not be used as an end-point since it was not at all sharp. Caffeine–sodium benzoate and quinine gave only one maximum corresponding to two equivalents of perchloric acid.

The duration of the titration varied with different titrating systems (in the presence of quinhydrone electrodes, from 30 min to 2 h; in the presence of antimony electrodes up to 40 min), because of the different rates of establishment of potential. The potential was most slowly attained in the titration of novalgin, but it is imperative to wait until the equilibrium state at the electrodes is reached, otherwise the titration end-point cannot be determined. This difficulty was not encountered in the titration of other substances.

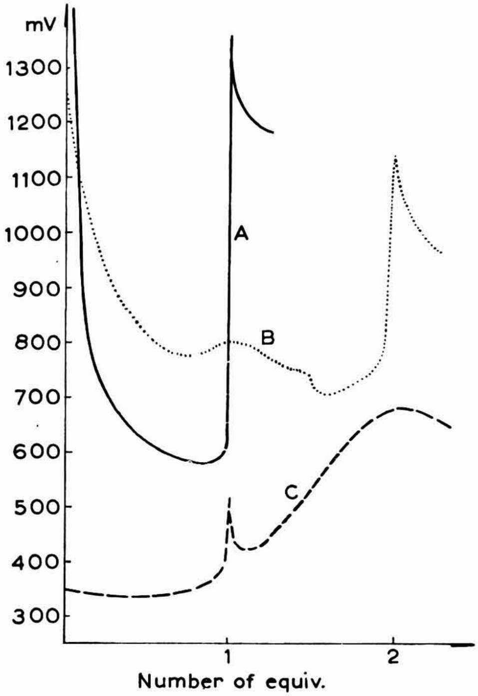


Fig. 4. Titration curves obtained with 0.1 *M* perchloric acid in the presence of quinhydrone electrodes: (A), 10^{-2} *M* solution of caffeine, resistance 50 kΩ; (B), 10^{-2} *M* solution of novalgin, resistance 10 kΩ; (C), 10^{-2} *M* solution of aminopyrine, resistance 80 kΩ.

TABLE 1

No.	*Sodium benzoate taken (g)*	*0.1 N $HClO_4$ consumed (ml)*	*Sodium benzoate found (g)*	*Solvent*
1	0.1000	6.91	0.0996	
2	0.1000	6.94	0.1000	
3	0.1000	6.94	0.1000	10 ml CH_3COOH +
4	0.1000	6.94	0.1000	10 ml $(CH_3CO)_2O$
5	0.1000	6.91	0.0996	
6	0.1000	6.92	0.0997	
7	0.1000	6.94	0.1000	
		Mean value:	0.0998 ± 0.0002[a]	
	Found by potentiometric titration:		0.0999	

[a] ± 0.0002 is the average deviation, $\frac{\Sigma|d|}{(n)}$.

TABLE 2

No.	Substance	Taken (g)	Found by potentiometric titration (g)	Derivative polarographic titrations				Solvent
				Antimony electrodes		Quinhydrone electrodes		
				No. of titrns.	Found (g)	No. of titrns.	Found (g)	
1	Aminopyrine	0.1500	0.1501	8	0.1499 ± 0.0003	15	0.1502 ± 0.0002	20 ml CH_3COOH
2	Antipyrine	0.1500	0.1506	6	0.1501 ± 0.0003	10	0.1505 ± 0.0002	10 ml CH_3COOH + 10 ml $(CH_3CO)_2O$
3	Brucine	0.2000	0.1988	2	0.1987 ± 0.0001	2	0.1987 ± 0.0001	10 ml CH_3COOH + 10 ml $(CH_3CO)_2O$
4	Cinchonine	0.1000	0.0942	3	0.0942 ± 0.0004	3	0.0943 ± 0.0001	10 ml CH_3COOH + 10 ml $(CH_3CO)_2O$
5	Diethylaniline	0.1484	0.1464	3	0.1463 ± 0.0001	4	0.1464 ± 0.0001	20 ml CH_3COOH
6	Isoniazide	0.1000	0.0998	11	0.0999 ± 0.0002	10	0.0997 ± 0.0001	20 ml CH_3COOH
7	Isopropyl phenazone	0.1500	0.1485	3	0.1848 ± 0.0000	6	0.1485 ± 0.0000	20 ml CH_3COOH
8	Narcotine	0.2000	0.1975	3	0.1970 ± 0.0001	3	0.1975 ± 0.0005	10 ml CH_3COOH + 10 ml $(CH_3CO)_2O$
9	Nicotinamide	0.1000	0.0997	3	0.0996 ± 0.0001	3	0.0996 ± 0.0001	10 ml CH_3COOH + 10 ml $(CH_3CO)_2O$
10	Potassium acetate	0.0859	0.0839	3	0.0834 ± 0.0000	2	0.0838 ± 0.0000	10 ml CH_3COOH + 10 ml $(CH_3CO)_2O$
11	Procaine-HCl	0.1500	0.1498	6	0.1497 ± 0.0002	13	0.1493 ± 0.0002	10 ml CH_3COOH + 10 ml 3% $Hg(CH_3COO)_2$ in CH_3COOH
12	Sodium benzoate	0.1000	0.0999	7	0.0999 ± 0.0003	10	0.1001 ± 0.0003	10 ml CH_3COOH + 10 ml $(CH_3CO)_2O$
13	Sodium *p*-amino-salicylate	0.2000	0.1999	6	0.1998 ± 0.0005	12	0.1998 ± 0.0003	20 ml CH_3COOH
14	Sodium formate	0.0500	0.0499	3	0.0501 ± 0.0001	4	0.0500 ± 0.0001	20 ml CH_3COOH
15	Sodium salicylate	0.1000	0.0997	2	0.0996 ± 0.0001	2	0.0997 ± 0.0000	10 ml CH_3COOH + 10 ml $(CH_3CO)_2O$
16	Tributylamine	0.1953	0.1609	3	c.1605 ± 0.0003	4	0.1608 ± 0.0002	10 ml CH_3COOH + 10 ml $(CH_3CO)_2O$
17	Triethylamine	0.0838	0.0813	2	0.0813 ± 0.0001	2	0.0813 ± 0.0001	10 ml CH_3COOH + 10 ml $(CH_3CO)_2O$
18	Triheptylamine	0.2969	0.2826	2	0.2826 ± 0.0005	3	0.2824 ± 0.0001	10 ml CH_3COOH + 10 ml $(CH_3CO)_2O$

A comparison of the results obtained by derivative polarographic titrations in the presence of antimony electrodes, with those obtained in the presence of quinhydrone electrodes show that a sharper end-point is obtained with quinhydrone electrodes (Fig. 5). The advantage of antimony electrodes is that there is a more rapid establishment of potential. For titrations of hydrochlorides of organic bases carried out in the presence of mercuric acetate, the antimony electrodes become amalgamated and consequently the potential is less rapidly established.

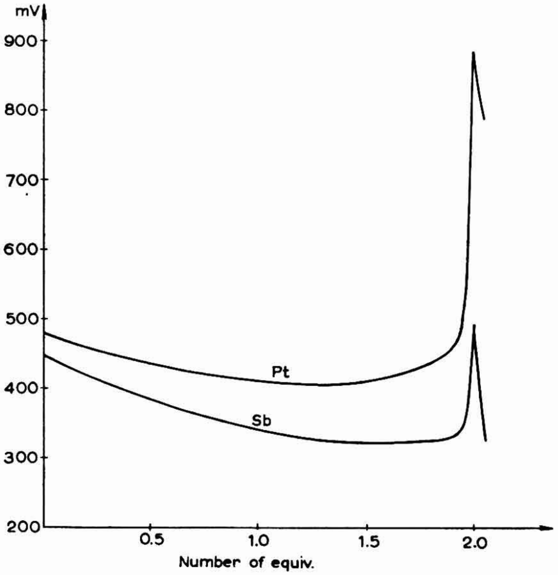


Fig. 5. Titration curves of $3 \cdot 10^{-2}$ *M* solution of cinchonine in the presence of two quinhydrone (Pt) or two antimony electrodes.

Derivative polarographic titrations give results of excellent reproducibility and high accuracy. For instance, Table 1 shows the results obtained in the determination of sodium benzoate by derivative polarographic titration with antimony electrodes. The results obtained using various titrating substances are given in Table 2.

ACKNOWLEDGEMENT

We thank MILIVOJE TOŠIĆ and MILORAD RANKOVIĆ for their help in carrying out the experimental part of this work.

SUMMARY

Derivative polarographic titration of some tertiary amines and salts of organic acids with perchloric acid in a mixture of glacial acetic acid and acetic anhydride, with two antimony or quinhydrone electrodes is described. The advantages of the method over potentiometric titration are that a sharper end-point is obtained and the use of a reference electrode and a salt bridge is avoided. The rather long time required for the titration of certain systems is a disadvantage. Quinhydrone electrodes give

sharper titration end-points than antimony electrodes, but titrations with the latter can be accomplished more rapidly. The results obtained are in very good agreement with those obtained by potentiometric titration and afford excellent reproducibility.

REFERENCES

1 C. N. Reilley, W. D. Cooke and N. H. Furman, *Anal. Chem.*, 23 (1951) 1223.
2 I. Shain and G. R. Svoboda, *Anal. Chem.*, 31 (1959) 1857.
3 J. W. Ross and I. Shain, *Anal. Chem.*, 28 (1956) 548.
4 G. A. Harlow, C. M. Noble and G. E. A. Wyld, *Anal. Chem.*, 28 (1956) 784.
5 G. R. Svoboda, *Anal. Chem.*, 33 (1961) 1638.
6 T. Enoki and K. Mirisaka, *Yakugaku Zasshi*, 77 (1957) 121; 125.
7 E. Bishop and G. D. Short, *Analyst*, 87 (1962) 467.
8 G. D. Short and E. Bishop, *Analyst*, 87 (1962) 724.
9 G. D. Short and E. Bishop, *Analyst*, 87 (1962) 860.
10 W. B. Mather, Jr. and F. C. Anson, *Anal. Chim. Acta*, 21 (1959) 468.
11 A. I. Vogel, *Quantitative Inorganic Analysis*, Longmans, London, 1961, p. 944.

DETERMINATION OF TERTIARY AMINES AND SALTS OF ORGANIC ACIDS, IN GLACIAL ACETIC ACID BY DEAD-STOP METHOD

VILIM VAJGAND AND TIBOR PASTOR

Faculty of Sciences, Institute of Chemistry, Belgrade (Yugoslavia)

(Received September 13th, 1963)

We have described in previous papers[1,2] the titration of tertiary amines in glacial acetic acid by the method of derivative polarographic titration. In that work we studied the behaviour of antimony and quinhydrone electrodes, particularly the rate of the potential establishment and also the changes of anode and cathode potential. We have now extended our investigations further to the examination of the use of these electrodes for the determination of the end-point by the dead-stop method. This is a useful method for analyses in non-aqueous media and is well known for its simplicity and accuracy.

In spite of its advantages, the dead-stop method has not often been applied to the titration of acids and bases. The first attempt in this direction was made by MANN[3], who carried out titrations of acids and bases in the presence of quinhydrone electrodes and used the method for the determination of the acid and saponification numbers of oils, in a mixture of alcohol and benzene. He also obtained good results in the titrations of organic acids and bases in the presence of quinhydrone when he replaced the platinum electrodes with aluminium electrodes. However, this method did not give satisfactory results in solutions containing chlorides, nitrates, nitrites and strong oxidizing agents. A further improvement in dead-stop titrations was made by ENOKI AND MIRISAKA[4], who used antimony electrodes.

Of the above mentioned electrodes we have found that both the quinhydrone and the antimony electrode are useful for titrations in glacial acetic acid because of their reversibility, rapid establishment of equilibrium and also because they are corroded by few organic solvents.

EXPERIMENTAL

The analyses were performed with the apparatus depicted in Fig. 1. The electromotive force e.m.f. necessary for the polarization of electrodes was obtained from a 2-V lead storage battery connected with a 100-Ω potentiometer, Elektrozveze PON 210. The changes of current during the titration were measured with a multiflex-type galvanometer, Radiometer GMV 13 b, the sensitivity of which was changed by connecting a potentiometer in parallel. Besides the electrodes described previously[1,2], tungsten and aluminium electrodes of small area, in the presence of quinhydrone, were also used in this titration.

The preparation of solvents, standard solution of perchloric acid and samples for titration have already been described in the previous work.

The curves obtained in titrations in acetic acid by the dead-stop method are similar in shape to those obtained in aqueous solutions; with antimony electrodes the titration end-point is indicated by the current minimum (Fig. 2a). The minima

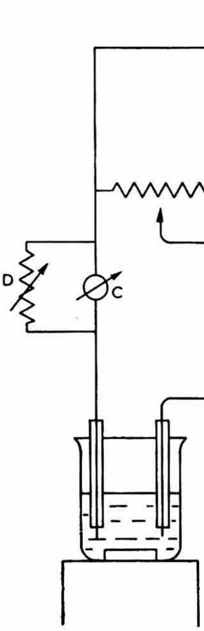


Fig. 1. A, lead accumulator; B, 100-Ω potentiometer; C, mirror galvanometer; D, 1-kΩ potentiometer.

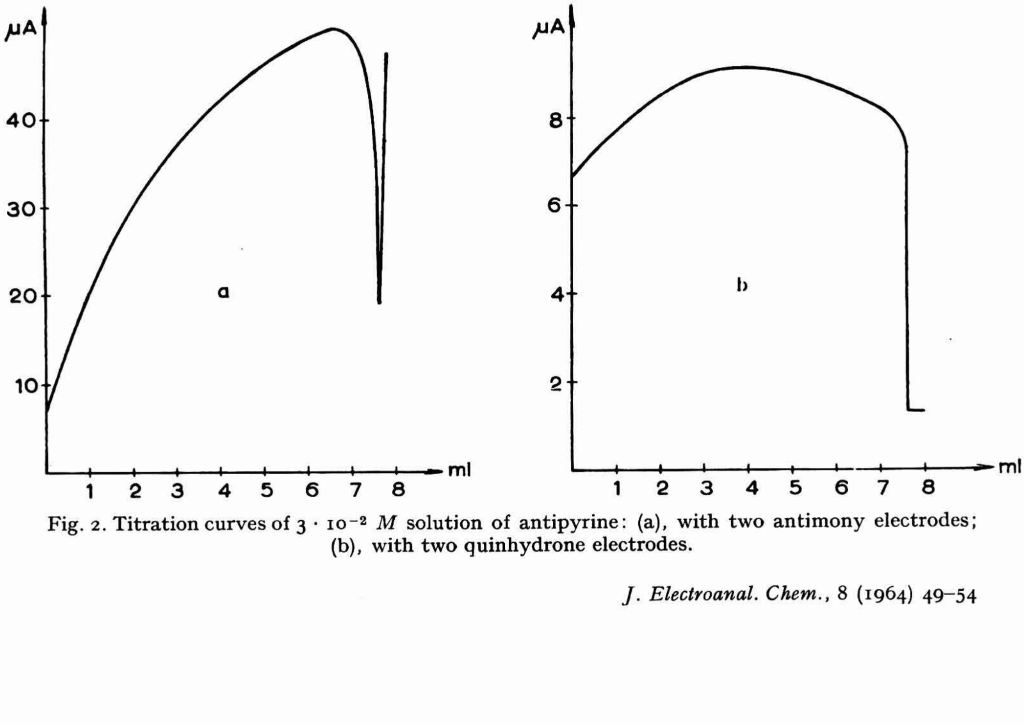


Fig. 2. Titration curves of $3 \cdot 10^{-2}$ *M* solution of antipyrine: (a), with two antimony electrodes; (b), with two quinhydrone electrodes.

obtained are clearly defined but their sharpness depends to a great extent on the composition of the solution used. An increase in the amount of acetic anhydride in the solvent mixture increases the sharpness of the titration end-point. This is illustrated by the curves obtained in the titration of antipyrine in the presence of various acetic acid–acetic anhydride mixtures. (Fig. 3). A similar effect was observed when

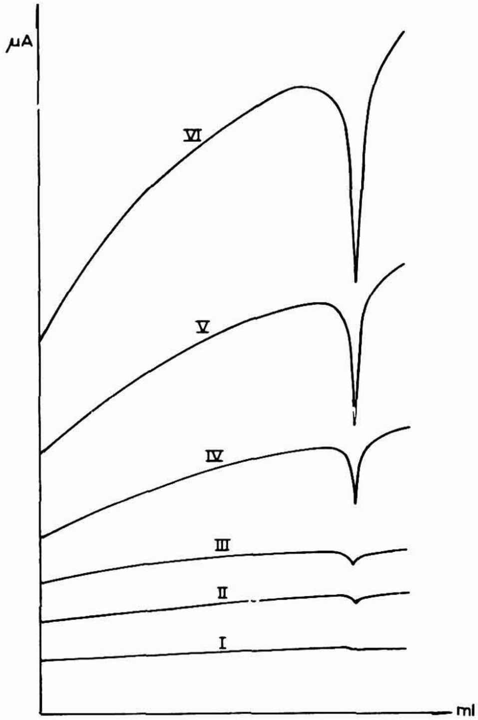


Fig. 3. Titration curves of $3 \cdot 10^{-2}$ *M* solution of antipyrine: (I), in pure glacial acetic acid; (II), (III), (IV), (V) and (VI), in solutions containing 10, 20, 40, 60 and 80%, respectively, of acetic anhydride.

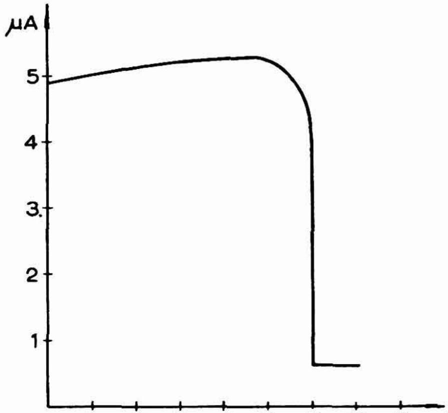


Fig. 4. Titration curves of $3 \cdot 10^{-2}$ *M* solution of sodium salicylate in the presence of quinhydrone with two tungsten electrodes.

quinhydrone electrodes were used, although the titration curves obtained by the use of quinhydrone electrodes are different in shape from those obtained with antimony electrodes. From the shape of the curve in Fig. 2b, it is apparent that the current rapidly decreases at the titration end-point, and then remains constant. During the titration in the presence of quinhydrone the current is stable up to the equivalence point. Towards the equivalence point it begins to change slowly and, to obtain the stationary state one has to wait 5–20 min after the addition of reagent. After the titration end-point, each addition of titrating agent effects a small rise in current, but after some time the current slowly decreases to a constant value. As a result, the titration with quinhydrone electrodes takes rather a long time. We tried to overcome this disadvantage by using tungsten or aluminium electrodes, but these were unsatisfactory. With tungsten electrodes, which give titration curves of similar shape as those obtained using platinum electrodes (Fig. 4), the stationary state was attained even more slowly; in the titrations carried out with aluminium electrodes the end-point was not sharply defined (Fig. 5).

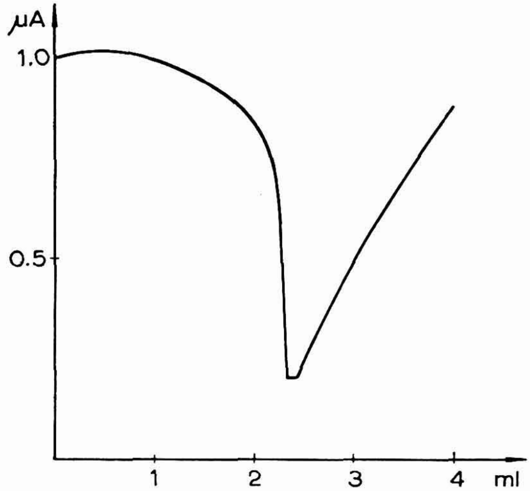


Fig. 5. Titration curve of $7 \cdot 10^{-3}$ *M* solution of narcotine in the presence of quinhydrone with two aluminium electrodes.

Besides the advantages of the dead-stop titration in glacial acetic acid, such as the stability of current in the course of titration and the sharpness of the titration end-point, antimony electrodes exhibit also some undesirable properties. For example, the titration of hydrohalides of organic bases in the presence of mercuric acetate causes the formation of antimony amalgam so that the electrode is very quickly corroded; in the titration of strychnine nitrate the current fluctuates continually until the vicinity of the equivalence point, and then at the end-point becomes steady and remains so. However, in the titration of Iversal (*p*-benzoquinone-guanylhydrazone-thiosemicarbazone), in spite of the formation of a precipitate (which is formed during the titration and is dissolved after the titration end-point), antimony electrodes gave good results, whereas the same titration was unsuccessful with quinhydrone electrodes.

TABLE 1

Titrated substance	*Taken (g)*	*Found by potentiometric titration (g)*	*Titrations by dead-stop method*				*Solvent*
			Antimony electrodes		*Quinhydrone electrodes*		
			No. of titrns.	*Found (g)*	*No. of titrns.*	*Found (g)*	
Antipyrine	0.1500	0.1476	4	0.1472 ± 0.0002[a]	3	0.1474 ± 0.0004[a]	10 ml CH_3COOH + 10 ml $(CH_3CO)_2O$
Sodium benzoate	0.1000	0.0983	3	0.0979 ± 0.0001	4	0.0978 ± 0.0001	10 ml CH_3COOH + 10 ml $(CH_3CO)_2O$
Iversal*	0.1000	0.0987	3	0.0991 ± 0.0001			10 ml CH_3COOH + 10 ml $(CH_3CO)_2O$
Nicotine	0.0811	0.0797	4	0.0799 ± 0.0001			10 ml CH_3COOH + 10 ml $(CH_3CO)_2O$
Strychnine nitrate	0.1000	0.0983	4	0.0984 ± 0.0002			10 ml CH_3COOH + 10 ml $(CH_3CO)_2O$
Potassium acetate	0.0633	0.0634	4	0.0633 ± 0.0001	4	0.0633 ± 0.0001	10 ml CH_3COOH + 10 ml $(CH_3CO)_2O$
Isoniazide	0.1000	0.0986	4	0.0983 ± 0.0002			10 ml CH_3COOH + 10 ml $(CH_3CO)_2O$
Sodium *p*-amino salicylate	0.1500	0.1475	4	0.1475 ± 0.0002	4	0.1479 ± 0.0002	10 ml CH_3COOH + 10 ml $(CH_3CO)_2O$
Sodium acetate	0.0822	0.0822	3	0.0818 ± 0.0001	3	0.0817 ± 0.0000	10 ml CH_3COOH + 10 ml $(CH_3CO)_2O$
Sodium salicylate	0.1000	0.0997	6	0.0995 ± 0.0001	5	0.0995 ± 0.0001	10 ml CH_3COOH + 10 ml $(CH_3CO)_2O$
Nicotinamide	0.1000	0.0998	3	0.0987 ± 0.0001	5	0.0985 ± 0.0002	10 ml CH_3COOH + 10 ml $(CH_3CO)_2O$
Cinchonine	0.1000	0.0942	4	0.0939 ± 0.0002	6	0.0937 ± 0.0001	10 ml CH_3COOH + 10 ml $(CH_3CO)_2O$
Narcotine	0.1000	0.0987	3	0.0983 ± 0.0003	4	0.0984 ± 0.0002	10 ml CH_3COOH + 10 ml $(CH_3CO)_2O$
Pyridoxine-HCl**	0.1500	0.1473			4	0.1479 ± 0.0003	10 ml 3% $Hg(CH_3COO)_2$ + 10 ml $(CH_3CO)_2O$
Endoiodine***	0.1500	0.1479			3	0.1478 ± 0.0001	10 ml 3% $Hg(CH_3COO)_2$ + 10 ml $(CH_3CO)_2O$

* *p*-benzoquinone-guanylhydrazone thiosemicarbazone

** 5-hydroxy-6-methyl-3,4-pyridinemethanol hydrochloride

*** 1,3-bis(trimethylamino)-2-propanol diiodide

[a] average deviation, $\frac{\Sigma|d|}{n}$

The potential difference between the electrodes was varied from 40–100 mV. It is possible to apply a smaller potential difference using a more sensitive galvanometer. The current strength measured in the titrations was only 0.1–50 μA because of the very high resistance of the titrated systems.

Using this method we have successfully titrated solutions in the concentration range $7 \cdot 10^{-3}$–$3 \cdot 10^{-2}$ M. Theobromine and novalgin could not be titrated by this method. The titrated systems and the results obtained are presented in Table 1. This table shows that the results obtained by the dead-stop method are in accordance with those obtained by potentiometric titrations, and that the reproducibility is excellent.

ACKNOWLEDGEMENT

We thank ALEXANDER CVIJETIĆ for his help in carrying out the experimental part of this work.

SUMMARY

In this work, compounds containing tertiary nitrogen and salts of organic acids were titrated with perchloric acid by a dead-stop method in a mixture of glacial acetic acid and acetic anhydride. With antimony electrodes the stationary state was quickly established, the current was stable and the end-point was indicated by a sharp minimum in the current. Titrations in the presence of quinhydrone electrodes required a longer time and at the titration end-point the current was sharply reduced to a value which remained constant on further titration.

The effect of various amounts of acetic anhydride on the sharpness of the end-point in the presence of antimony, and quinhydrone electrodes has also been studied.

REFERENCES

1 V. VAJGAND AND T. PASTOR, *Glasnik Hem. Drustva, Beograd (Bull. Soc. Chim., Belgrade)*, 27 (1962) 263.
2 V. VAJGAND AND T. PASTOR, *Glasnik Hem. Drustva, Beograd*, 28 (1963) 1.
3 G. MANN, *Magy. Kem. Folyoirat*, 61 (1955) 26.
4 T. ENOKI AND K. MIRISAKA, *Yakugaku Zasshi*, 77 (1957) 121, 123, 125.

ELECTROCHEMICAL BEHAVIOR OF COPPER IONS AND SILVER ION IN HYDRACRYLONITRILE AND SOME RELATED NITRILES

FLOYD FARHA, JR. AND REYNOLD T. IWAMOTO

Department of Chemistry, University of Kansas, Lawrence, Kansas (U.S.A.)

(Received March 11th, 1964)

Voltammetry has been used to study the solvation of copper ions and silver(I) ion in a variety of nitriles[1-3] and alcohols[4,5]. In nitriles, the electrochemical reduction of copper(II) ion to the metal proceeds in two separate steps. This behavior of copper ions in nitriles is in contrast to that in water, in which copper(II) ion is reduced directly to the metal in one step, and is attributable to the combined effect of higher solvation energy of copper(I) ion and lower solvation energy of copper(II) ion in these solvents than in water. In the alcohols, copper(II) ion is reduced to the metal, also in two separate one-electron steps, but the behavior of copper ions is due solely to the lower solvation energy of copper(II) ion in these solvents than in water. Hydracrylonitrile possesses two active functional groups, the OH-group and the $C{\equiv}N$-group, through which it could solvate metal ions. In addition, this solvent has two conformers (*gauche* and *trans*) in equilibrium in the liquid state and a third (*cis*) that is obtainable, which could participate in the solvation of metal ions. The nature of solvated metal ions, particularly copper ions, in hydracrylonitrile and related nitriles, therefore, is of considerable interest. Use has been made of the potential of the copper(II)–copper(I) couple and that of the copper(I)–copper couple in these solvents to investigate this problem. Infrared and visible spectral studies have been carried out, and the results substantiate the information obtained from the electrochemical study.

Because the chemistry of silver(I) ion and of copper(I) ion, in general, are similar, the electrochemical behavior of silver(I) ion in hydracylonitrile and related nitriles has been examined and compared with that of copper(I) ion in the same solvents.

EXPERIMENTAL

The organic solvents were purified by treatment with appropriate reagents and fractional distillation. Absolute methanol, ethanol, 1-propanol, and 1-butanol were treated with calcium hydride and sodium borohydride, refluxed for an hour, then fractionally distilled. Hydracrylonitrile, 3-methoxypropionitrile, 3-ethoxypropionitrile, 3-isopropoxypropionitrile, 3-butenenitrile, and 3-chloropropionitrile were passed through a 2.5-cm (i.d.) × 35 cm column of neutral Woelm chromatographic alumina, activity grade 1, and fractionally distilled under reduced pressure. Acetoni-

TABLE 1

ELECTROCHEMICAL BEHAVIOR OF COPPER IONS IN HYDRACRYLONITRILE, SOME RELATED NITRILES, AND OTHER PERTINENT SOLVENTS[a, b, c, d]

g	*Solvent*	*Et_4NClO_4 (Supporting electrolyte)*				*$LiClO_4$ (Supporting electrolyte)*			
		$E_{\frac{1}{2}Cu(II),Cu(I)}$	$\frac{0.059}{n}$	$E^{\circ\prime}_{Cu(I),Cu}$	$\frac{0.059}{n}$	$E_{\frac{1}{2}Cu(II),Cu(I)}$	$\frac{0.059}{n}$	$E^{\circ\prime}_{Cu(I),Cu}$	$\frac{0.059}{n}$
65	Hydracrylonitrile	+0.89	0.082	−0.32	0.084	+0.92	0.065	−0.32	0.059
32	1 : 1 Ethanol–acetonitrile[e]	+0.60	0.12	−0.32	0.069	+0.62	0.11	−0.32	0.063
	1 : 1 1-Butanol–propionitrile[e]	+0.69	0.080	−0.31	0.060	+0.69	0.084	−0.32	0.057
42	3-Methoxypropionitrile	+0.88	0.10	−0.34	0.059	+0.88	0.093		
34	3-Ethoxypropionitrile	+0.89	0.074	−0.34	0.063				
30	3-Isopropoxypropionitrile	+0.90	0.074	−0.34	0.069				
32	3-Butenenitrile	+0.91[f]	0.077[f]	−0.38	0.067				
45	3-Chloropropionitrile	+0.98	0.062	−0.32	0.063				
37	Acetonitrile	+0.96	0.070	−0.34	0.064	+0.92	0.074	−0.38	0.061
27	Propionitrile	+0.87	0.067	−0.39	0.059				
	1 : 1 Hydracrylonitrile–acetonitrile[e]	+0.86	0.084	−0.31	0.055				
24	Ethanol					+0.26[h]		+0.20[h]	
17	1-Butanol					+0.39	0.078	+0.22	0.059
				$E_{\frac{1}{2}Cu(I),Cu(Hg)}$				$E_{\frac{1}{2}Cu(I),Cu(Hg)}$	
	Hydracrylonitrile			−0.32	0.060			−0.30	0.052
	1 : 1 1-Butanol–propionitrile[e]			−0.34	0.060			−0.34	0.061
	3-Methoxypropionitrile			−0.36	0.057			−0.36	0.058
	3-Ethoxypropionitrile			−0.36	0.056				
	3-Isopropoxypropionitrile			−0.36	0.058				
	3-Butenenitrile			−0.39	0.057				
	3-Chloropropionitrile			−0.34	0.059				
	Acetonitrile			−0.38	0.059			−0.39	0.054
	Propionitrile			−0.40	0.058				
	1 : 1 Hydracrylonitrile–acetonitrile[e]			−0.35	0.059				
	Ethanol					+0.28[g]		+0.17[h]	
	1-Butanol					+0.31	0.059	+0.21	0.060

---

[a] All solutions are 0.1 M in supporting electrolyte. [b] All E-values are *vs.* S.C.E. [c] All E-and 0.59/n-values are the average of two or more runs. [d] Each E-value has been corrected for junction potential difference between the solvent system *vs.* S.C.E. and aqueous lithium perchlorate solution *vs.* S.C.E. (see RESULTS). [e] Equimolar mixture. [f] Value from one run. [g] Dielectric constant. [h] Reference 4.

trile was dried over and distilled from phosphorus pentoxide. Propionitrile was distilled first from calcium hydride, then from a small amount of phosphorus pentoxide. Allyl alcohol was dried over anhydrous potassium carbonate and fractionally distilled after filtration from the potassium carbonate.

Anhydrous lithium perchlorate, hexa-aquo-copper(II) perchlorate, and anhydrous silver perchlorate (all G. F. Smith Chemical Co. products) were dried in a vacuum oven at 70° and stored over anhydrous magnesium perchlorate. Analysis showed the copper salt to be the dihydrate. Tetraethylammonium perchlorate was prepared by neutralizing a 10% tetraethylammonium hydroxide solution (Eastman) with reagent-grade 70% perchloric acid, recrystallizing six times from water, and drying in a vacuum oven at 70°. Tris(4,7-dimethyl-1,10-phenanthroline)iron(II) perchlorate was prepared as described previously[6].

Current–voltage curves were obtained with a Kelley–Jones–Fisher[7] controlled-potential polarograph. All solutions were examined at 25 ± 1°. An H-type polarographic cell was used, with either a dropping mercury electrode or a rotating platinum electrode in one side arm. A saturated calomel electrode and a platinum-foil electrode, to function as the auxiliary electrode in a three-electrode system, were placed in the other side arm. A *ca.* 1-cm length of 22-gauge platinum wire extending from the tip of a soft-glass tubing rotated at *ca.* 600 r.p.m. served as the rotating platinum electrode.

One-tenth molar (0.10 *M*) tetraethylammonium perchlorate or lithium perchlorate solutions *ca.* $5 \cdot 10^{-4}$ *M* in copper(II) perchlorate were used in the electrochemical study. They were deoxygenated with purified nitrogen and protected from atmospheric oxygen during the course of measurement by passing nitrogen over the surface.

A calibration curve of dielectric constant *vs.* capacitance reading of a Sargent Model V chemical oscillometer was used to obtain the dielectric constant of hydracrylonitrile, 3-methoxypropionitrile, 3-ethoxypropionitrile, 3-isopropoxypropionitrile, 3-butenenitrile, 3-chloropropionitrile and the 1 : 1 ethanol–acetonitrile mixture.

Visible spectral data were obtained with a Cary Model 14 recording spectrophotometer, and the infrared spectral data with a Perkin–Elmer Model 421 spectrophotometer.

RESULTS

Table 1 summarizes the pertinent electrochemical data on the behavior of copper ions at the dropping mercury electrode and at the rotating platinum electrode in hydracrylonitrile, in several related nitriles, and in other solvents of importance to this study. Similar information for silver(I) ion is presented in Table 2. Each potential has been corrected to adjust for differences in liquid-junction potential among the solvents[6].

$E_{\text{corr.}} = E_{\frac{1}{2}\ \text{oxid. of tris(4,7-dimethyl-1,10-phenanthroline)iron(II)}}\ (\text{aqueous LiClO}_4) - E_{\frac{1}{2}\ \text{oxid. of tris(4,7-dimethyl-1,10-phenanthroline)iron(II)}}\ (\text{solvent}).$

Aqueous lithium perchlorate solution is the reference solvent. Table 3 contains the half-wave potentials for the oxidation of tris(4,7-dimethyl-1,10-phenanthroline)iron(II) in the solvents used in this investigation.

The infrared and visible spectral data are summarized in Table 4 and 5, respectively.

TABLE 2

ELECTROCHEMICAL BEHAVIOR OF SILVER ION IN HYDRACRYLONITRILE, SOME RELATED NITRILES, AND OTHER PERTINENT SOLVENTS[a, b, c, d]

Solvent	*Et_4NClO_4 (Supporting electrolyte)*		*$LiClO_4$ (Supporting electrolyte)*	
	$E^{\circ\prime}_{Ag(I),Ag}$	$\frac{0.059}{n}$	$E^{\circ\prime}_{Ag(I),Ag}$	$\frac{0.059}{n}$
Hydracrylonitrile	+0.34	0.075	+0.33	0.068
1 : 1 Ethanol–acetonitrile[e]	+0.26	0.069	+0.23	0.075
1 : 1 1-Butanol–propionitrile[e]	+0.31	0.069	+0.32	0.063
3-Methoxypropionitrile	+0.29	0.052	+0.28	0.070
3-Ethoxypropionitrile	+0.30	0.054		
3-Isopropoxypropionitrile	+0.30	0.056		
3-Butenenitrile	+0.31	0.060		
3-Chloropropionitrile	+0.30[f]	0.071		
Acetonitrile	+0.30	0.069	+0.27	0.059
Propionitrile	+0.27	0.059		
Acrylonitrile	+0.36[f]	0.064		
Allyl alcohol			+0.40	0.058
Methanol			+0.49	0.080
Ethanol			+0.50	0.068
1-Propanol			+0.50	0.070
H_2O			+0.49	0.062
	$E_{\frac{1}{2}Ag(I),Ag(Hg)}$		$E_{\frac{1}{2}Ag(I),Ag(Hg)}$	
Acetonitrile	+0.37	0.050		
3-Methoxypropionitrile	+0.38	0.055	+0.38	0.050
3-Ethoxypropionitrile	+0.38	0.059		
3-Isopropoxypropionitrile	+0.39	0.060		
3-Butenenitrile	+0.34	0.059		
3-Chloropropionitrile	+0.40	0.058		
Propionitrile	+0.34	0.054		
Acrylonitrile	+0.39	0.080		

[a] All solutions are 0.1 *M* in supporting electrolyte. [b] All *E*-values are *vs.* S.C.E. [c] All *E*- and 0.059/*n*-values are the average of two or more runs. [d] Each *E*-value has been corrected for junction potential difference between the solvent system *vs.* S.C.E. and aqueous lithium perchlorate solution *vs.* S.C.E. (see RESULTS). [e] Equimolar mixture. [f] Value from one run.

DISCUSSION

The potentials for the copper couples in water are:

$$Cu^{+} + e = Cu; \quad E^{\circ} = +0.28 \text{ V } vs. \text{ S.C.E.}$$

$$Cu^{2+} + e = Cu^{+}; \quad E^{\circ} = -0.09 \text{ V } vs. \text{ S.C.E.}$$

These potentials and those in acetonitrile and in ethanol for the two couples indicate (i) that the solvation energy of copper(I) ion in acetonitrile is much greater than that in water, and in ethanol about equal to that in water, and (ii) that the solvation energy of copper(II) ion is less both in acetonitrile and in ethanol than in water. Quantitatively, the solvation energy of copper(I) ion is the equivalent of 0.58 V [the difference between $E^{\circ\prime}_{Cu(I),Cu}$ (ethanol–$LiClO_4$) and $E^{\circ\prime}_{Cu(I),Cu}$ (acetonitrile–$LiClO_4$)] greater in acetonitrile than in ethanol, and that of copper(II) ion is the equivalent of 0.1 V greater in ethanol than in acetonitrile. The latter value is obtained by adding 0.58 V to the potential of the copper(II)–copper(I) couple in ethanol and evaluating the difference between this calculated value for the copper(II)–copper(I) couple in

TABLE 3

HALF-WAVE POTENTIALS FOR THE OXIDATION OF TRIS(4,7-DIMETHYL-1,10-PHENANTHROLINE)-IRON(II) PERCHLORATE

Solvent system	$E_{\frac{1}{2}}$ *vs. S.C.E.*	*0.059/n*
Solvent (0.1 M Et_4NClO_4)		
Hydracrylonitrile	+0.795	0.060
1 : 1 Ethanol–acetonitrile	+0.975	0.053
1 : 1 Butanol–propionitrile	+0.945	0.059
3-Methoxypropionitrile	+0.940	0.060
3-Ethoxypropionitrile	+0.975	0.062
3-Isopropoxypropionitrile	+0.985	0.062
3-Butenenitrile	+0.965	0.060
3-Chloropropionitrile	+0.920	0.065
Acetonitrile	+0.895[a]	0.060
Propionitrile	+0.960	0.063
1 : 1 Hydracrylonitrile–acetonitrile	+0.820	0.055
Acrylonitrile	+0.945	0.059
Solvent (0.1 M $LiClO_4$)		
Hydracrylonitrile	+0.785	0.050
1 : 1 Ethanol–acetonitrile	+0.965	0.053
1 : 1 1-Butanol–propionitrile	+0.945	0.059
3-Methoxypropionitrile	+0.935	0.055
Acetonitrile	+0.860[a]	0.063
Allyl alcohol	+0.890[a]	0.077
Methanol	+0.890[a]	0.058
Ethanol	+0.895[a]	0.06
1-Propanol	+0.915[a]	0.06
1-Butanol	+0.920[a]	0.06
Water	+0.830[a]	0.06

[a] Taken from reference 6.

TABLE 4

INFRARED SPECTRAL DATA

Medium	ν_{OH} *(stretching) (cm^{-1})*	$\nu_{C \equiv N}$ *(stretching) (cm^{-1})*
Acetonitrile		2254
Acetonitrile + $Cu(ClO_4)_2 \cdot 2\ H_2O$[a]		2299
Hydracrylonitrile	3420 (broad)	2250
Hydracrylonitrile + $Cu(ClO_4)_2 \cdot 2\ H_2O$[a]	3420 (broad) unchanged	2300
1 : 1 Ethanol–acetonitrile	3420 (broad)	2257
1 : 1 Ethanol–acetonitrile + $Cu(ClO_4)_2 \cdot 2\ H_2O$[a]	3420 (development of a broad shoulder on the lower frequency side of the band)	2257
1 : 1 Hydracrylonitrile–acetonitrile + $Cu(ClO_4)_2 \cdot 2\ H_2O$[a]	3420 (broad)-unchanged	2300

[a] 0.1 *M* in $Cu(ClO_4)_2 \cdot 2\ H_2O$.

a hypothetical system in which copper(II) ion is solvated by ethanol and copper(I) ion is solvated by acetonitrile, and that for $E^{\circ\prime}_{Cu(II),Cu(I)}$ in acetonitrile.

On the basis of this information, one would expect copper(I) ion in hydracrylonitrile to be solvated completely by the nitrile group and copper(II) ion completely or almost completely by the hydroxyl group. If this were the case, the potential of the copper(I)–copper couple in hydracrylonitrile would be practically identical with that in acetonitrile or propionitrile and the potential of the copper(II)–copper(I) couple would be the same as that previously calculated for the hypothetical system in which copper(II) ion is solvated by ethanol and copper(I) ion by acetonitrile. Essentially identical potentials for the copper(I)–copper couple in hydracrylonitrile and acetonitrile indicate that copper(I) ion in hydracrylonitrile is indeed solvated by the nitrile group. The potentials for the copper(II)–copper(I) couple in hydracrylonitrile ($E^{\circ\prime} = +0.92$ V), in acetonitrile ($E^{\circ\prime} = +0.92$ V), and in the hypothetical solvent system previously discussed ($E^{\circ\prime} = +0.84$ V) suggest, however, that copper(II) ion, contrary to the information just derived, is solvated by hydracrylonitrile also through the nitrile group. On the other hand, in 1 : 1 mixtures (on a molar basis) of ethanol and acetonitrile and of 1-butanol and propionitrile, the potential of the copper(II)–copper(I) couple indicates that copper(II) ion is solvated, as expected, by the alcohol instead of the nitrile. Visible and infrared spectral data confirm this unusual situation. The visible spectrum of a hydracrylonitrile solution of copper(II) perchlorate has an absorption band at 760–770 mμ, identical with those in the spectra of acetonitrile and of propionitrile solutions, and that of 1 : 1 ethanol–acetonitrile solution of copper(II) perchlorate has an absorption band at 810–815 mμ, identical with those in the spectra of ethanol and of 2-propanol solutions. In the infrared spectral region, a hydracrylonitrile solution of copper(II) perchlorate has a broad absorption band at *ca.* 3420 cm^{-1}, identical with that in the spectrum of hydracrylonitrile, and a new C$\equiv$N band at 2300 cm^{-1}, 50 cm^{-1} higher than the C$\equiv$N stretching band in hydracrylonitrile. The new C$\equiv$N band appears at the same frequency at which a similar band appears in acetonitrile solutions of copper(II) perchlorate as a result of copper(II) ion–nitrile interaction. For 1 : 1 ethanol–acetonitrile solution of copper(II) perchlorate, however, the C$\equiv$N stretching band is unaffected and the OH stretching band has a broad shoulder on the lower frequency side of the band, indicating participation of ethanol in the solvation of copper(II) ion.

The solvation of copper(II) ion by hydracrylonitrile through the nitrile group rather than the oxygen atom of the hydroxyl group as in 1 : 1 ethanol–acetonitrile and 1 : 1 1-butanol–propionitrile mixtures can be accounted for if the extent of hydrogen bonding in hydracrylonitrile were much greater than in the alcohol–nitrile mixtures. Extensive hydrogen bonding would decrease the availability of oxygen sites for solvation of copper(II) ion, favoring solvation by the nitrile group. From the OH stretching region of the infrared spectra of hydracrylonitrile and of the 1 : 1 nitrile–alcohol mixtures, hydrogen bonding in these two solvent systems, however, appears to be practically the same. Except for a factor of two difference in absorbancy, the band position and shape are identical. Because the number of hydroxyl-containing molecules in the 1 : 1 alcohol–nitrile mixture is approximately one-half that in hydracrylonitrile, the absorbancy of the OH stretching band in the mixtures is expected to be only one-half of that in hydracrylonitrile. Preferential solvation of copper(II) ion by the nitrile group in hydracrylonitrile, however, is not due to this solvent having twice as many hydroxyl-containing solvent molecules as the alcohol–nitrile mixtures, because electrochemical and spectral studies of 1 : 1 hydracrylonitrile–acetonitrile solutions of copper(II) ion show that in this latter mixture divalent copper ion is solvated also by the nitrile group.

We offer the following explanation for the different modes of solvation of copper(II) ion by hydracrylonitrile and by 1 : 1 alcohol–nitrile mixtures. Because of the polar nature of the solvent, in hydracrylonitrile the solvent molecules in the co-ordination sphere of copper(II) ion are oriented with the less polar end (the nitrile group) co-ordinated to copper(II) ion and the more polar end (the hydroxyl group) sticking out and forming a polar outer sheath. Although the stability of this copper(II) species is less than if the hydracrylonitrile molecules were arranged in the co-ordination sphere with the oxygen atom of the hydroxyl group attached to copper(II) ion, the decrease in stability of the solvated copper(II) ion is adequately compensated for by greater interaction between the solvent and the solvated copper(II) ion. In alcohol–nitrile mixtures, the polar solvated system likewise favors the more polar solvated species. But, in this case, alcohol-solvated copper(II) ion with an outer sheath containing OH groups is more polar than nitrile-solvated copper(II) ion with an outer sheath consisting only of alkyl groups. To check this explanation, visible spectral studies with nitromethane and 1,2-dichloroethane solutions were carried out. The results are summarized in Table 5. The shift in the absorption band from 760–770 mμ for hydracrylonitrile solutions of copper(II) ion and from 780 mμ for nitromethane solutions of copper(II) ion 0.5 *M* in hydracrylonitrile to 805 mμ for 1,2-dichloroethane solutions of copper(II) ion 0.5 *M* in hydracrylonitrile, and from 800 mμ for nitromethane solutions of copper(II) ion 0.25 *M* in ethanol and 0.25 *M* in acetonitrile to 795 mμ for 1,2-dichloroethane solutions of copper(II) ion 1 *M* in ethanol and 1 *M* in acetonitrile is in accord with the explanation. 1,2-Dichloroethane, a less polar medium than hydracrylonitrile or nitromethane, favors the less polar form of hydracrylonitrile-solvated copper(II) ion, the one in which copper(II) ion is co-ordinated to the oxygen atom of the hydroxyl group. With the mixtures containing ethanol and acetonitrile, in polar nitromethane medium (dielectric constant, 36) the polar ethanol-solvated copper(II) ion is the favored form, whereas in less polar 1,2-dichloroethane medium (dielectric constant, 10) the non-polar acetonitrile-solvated copper(II)

TABLE 5

VISIBLE SPECTRAL DATA FOR $Cu(ClO_4)_2 \cdot 2\ H_2O$ SOLUTIONS[a]

Medium	*$\lambda_{max.}$ (mμ)*
Acetonitrile	760–770
Propionitrile	760–770
Hydracrylonitrile	760–770
Ethanol	815
2-Propanol	815
1 : 1 Ethanol–acetonitrile	815
1 : 1 Hydracrylonitrile–acetonitrile	760–770
Nitromethane, 1 *M* ethanol	805
Nitromethane, 1 *M* acetonitrile	770
Nitromethane, 0.5 *M* hydracrylonitrile	780
Nitromethane, 0.25 *M* ethanol and 0.25 *M* acetonitrile	800
1,2-Dichloroethane, 1 *M* ethanol	805
1,2-Dichloroethane, 1 *M* acetonitrile	780
1,2-Dichloroethane, 0.5 *M* hydracrylonitrile	805
1,2-Dichloroethane, 1 *M* ethanol and 1 *M* acetonitrile	795

[a] 0.04 *M* solutions.

ion is the favored species. One can account for the solvation of copper(II) ion by acetonitrile in 1,2-dichloroethane containing ethanol and acetonitrile as due to the low dielectric constant medium favoring extensive hydrogen bonding between or among ethanol molecules making them less available for solvation of copper(II) ion. However, the visible spectrum of dichloroethane solutions of copper(II) ion containing hydracrylonitrile indicates that this is not the primary reason. In 1,2-dichloroethane solution of copper(II) ion 0.5 *M* in hydracrylonitrile, hydrogen bonding is expected to be just as extensive, but the absorption band for solvated copper(II) ion occurs at 805 mμ, indicating that the increase in the extent of hydrogen bonding because of the lowering of the dielectric constant of the medium is not sufficient to prevent preferential solvation of copper(II) ion by the hydroxyl group.

Although the *gauche* conformers are present in the liquid state and the *cis* conformers are obtainable, the fact that the potentials of each copper couple in hydracrylonitrile and the three alkoxypropionitriles are identical and the visible and infrared spectral data for hydracrylonitrile solutions indicate that these conformers are not the forms of hydracrylonitrile or the three alkoxypropionitriles involved in the solvation of copper ions. If the *gauche* or *cis* conformer were involved, considerable solvent effect would have been observed as a result of intramolecular and intermolecular interactions of solvent molecules in the co-ordination sphere because of differences in size among the hydrogen and the alkyl portions of the HO-and RO-groups in the four substituted propionitriles.

3-Butenenitrile, which has two functional groups (an olefinic group and a nitrile group) capable of solvating copper(I) ion, is also an interesting solvent. The potentials for the copper(I)–copper and copper(I)–copper amalgam couples show clearly that the solvation energy of copper(I) ion in 3-butenenitrile is similar to that of copper(I) ion in propionitrile, and, therefore, that copper(I) ion is solvated by 3-butenenitrile through the nitrile group rather than the olefinic group. The slightly positive values of the two copper(I)–copper couples and the copper(II)–copper(I) couple in 3-butenenitrile compared to those in propionitrile can be attributed to the lower basicity of the nitrile group in 3-butenenitrile than in propionitrile. This character of the nitrile group in 3-butenenitrile is in accord with the more acidic nature of 3-butenoic acid compared with that of butanoic acid ($K_{\text{3-butenoic acid}}/K_{\text{butanoic acid}}=2.55$)[8].

The more positive potentials of the copper(II)–copper(I) couple and the copper(I)–copper or the copper(I)–copper amalgam couple in 3-chloropropionitrile than in propionitrile reflects the decrease in basicity of 3-chloropropionitrile resulting from the electron-withdrawing inductive effect of the chlorine atom on the nitrile group. A similar inductive effect of the substituents in the 3-position on the nitrile group in hydracrylonitrile, methoxypropionitrile, ethoxypropionitrile, and isopropoxypropionitrile accounts undoubtedly for the more positive potentials for the two copper(I)–copper couples and for the slightly more positive potentials of the copper(II)–copper(I) couple in these nitriles than in propionitrile. With regard to the potentials of the copper(II)–copper(I) couple in these 3-substituted nitriles, decrease in solvation energy of copper(I) ion should shift the potential of the copper(II)–copper(I) couple to negative values, but this effect is compensated for by a decrease also in the solvation energy of copper(II) ion, which shifts the potential of the copper(II)–copper(I) couple to positive values. This analysis of the basic character of the substituted nitriles is consistent with the more acidic character (as indicated by the pK values) of 3-chloropropionic acid (pK = 4.02) and 3-hydroxypropionic acid (pK = 3.73) than of propionic acid (pK = 4.88).

Interestingly, the electrochemical data reveal no pronounced effect of ion-pair formation between cations and perchlorate ions in these nitriles. For example, the formation constants in acetonitrile[9] of $10^{1.05}$ for Et_4N^+, ClO_4^-; $10^{2.8}$ for Li^+, picrate$^-$; and $< 10^{1.0}$ for Et_4N^+, picrate$^-$ indicate that the extent of ion-pair formation between lithium ion and perchlorate ion is greater than between tetraethylammonium ion and perchlorate ion and, therefore, the concentration of free perchlorate ion is much higher in the tetraethylammonium perchlorate solution of a given nitrile than in the lithium perchlorate solution. The potentials of the copper couples in tetraethylammonium perchlorate solutions, however, show no tendency to be more negative than those in lithium perchlorate solutions. In addition, in spite of a decrease in the dielectric constant of the solvent in the series methoxypropionitrile, ethoxypropionitrile, and isopropoxypropionitrile, the potentials of the copper(II)–copper(I) and of the two copper(I)–copper couples in these nitriles do not reflect any increase in the extent of ion-pair formation between each of the copper ions and perchlorate ion. In fact, the potential of the copper(II)–copper(I) couple shifts in the opposite direction from that expected on the basis of increase ion-pair formation between copper(II) ion and perchlorate ion as one moves down the series from methoxypropionitrile to isopropoxypropionitrile.

Except for the fact that silver(I) ion is reduced at potentials more positive than those at which copper(I) ion is reduced, the data in Table 2 on the electrochemical behavior of silver(I) ion are similar to those for copper(I) ion. The potentials of the silver couples show that the same factors which govern the solvating ability of the nitriles for copper(I) ion influence the solvating ability of the nitriles for silver(I) ion. Some interesting features of the data are: (i) the identical potentials for the reduction of silver(I) ion in water and in the alcohols; (ii) the greater ease of reduction of silver ion at the dropping mercury electrode because of amalgam formation than at the rotating platinum electrode, and (iii) the more negative potential at which silver(I) ion is reduced in allyl alcohol than in 1-propanol, which indicates that the olefinic group in the alcohol is involved in the solvation of silver(I) ion. Participation of the olefinic group in the solvation of silver(I) ion in allyl alcohol is not surprising since silver(I)–allyl alcohol complexes have been reported in the literature[10,11].

ACKNOWLEDGEMENT

We are indebted to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of the initial phase of this research and to the Directorate of Chemical Sciences, Air Force Office of Scientific Research (AFOSR Grant 220-63) and the University of Kansas (General Research Fund) for support of the final phase.

SUMMARY

The electrochemical behavior of copper ions in hydracrylonitrile and related nitriles has been investigated. It is of interest to note that in hydracrylonitrile copper(II) ion is solvated by the nitrile group, whereas in 1 : 1 alcohol–nitrile mixtures, it is solvated by the hydroxyl group. This unusual situation appears to be due to the fact that hydracrylonitrile (dielectric constant, 65), 1 : 1 ethanol–acetonitrile mixture (di-

electric constant, 32), and 1 : 1 1-butanol–propionitrile mixture are polar solvent systems and, therefore, favor the more polar solvated form of copper(II) ion. This, in hydracrylonitrile has the solvent molecules oriented with the nitrile group attached to copper(II) ion and the hydroxyl group sticking out and forming a polar outer sheath and in 1 : 1 alcohol–nitrile mixture has alcohol rather than nitrile molecules in the co-ordination sphere. Nitrile-solvated copper(II) ion with an outer sheath consisting only of alkyl groups behaves like a non-polar solute.

In view of the absence of any solvent effect on the potentials of the copper couples in hydracrylonitrile, 3-butenenitrile, and in the alkoxypropionitriles, copper ions are most likely solvated by the *trans* conformer of these solvents. The effect of substituents in the 3-position in propionitrile *i.e.*, on the basicity of the nitrile group on the potentials of the copper couples, is consistent with the influence of the substituents on other functional groups in different compounds.

Except for the fact that silver(I) ion is reduced at potentials more positive than those at which copper(I) ion is reduced, the electrochemical reduction of silver(I) ion in hydracrylonitrile and related nitriles is similar to that of copper(I) ion.

REFERENCES

1 I. M. Kolthoff and J. F. Coetzee, *J. Am. Chem. Soc.*, 79 (1957) 870, 1825.
2 A. I. Popov and D. H. Geske, *J. Am. Chem. Soc.*, 79 (1957) 2074.
3 R. C. Larson and R. T. Iwamoto, *J. Am. Chem. Soc.*, 82 (1960) 3239, 3526.
4 I. V. Nelson and R. T. Iwamoto, *Inorg. Chem.*, 1 (1962) 151.
5 I. V. Nelson, R. C. Larson and R. T. Iwamoto, *J. Inorg. Nucl. Chem.*, 22 (1961) 279.
6 I. V. Nelson and R. T. Iwamoto, *Anal. Chem.*, 35 (1963) 867.
7 M. T. Kelley, H. C. Jones and H. C. Fisher, *Anal. Chem.*, 31 (1959) 1475.
8 J. F. J. Dippy, *Chem. Rev.*, 25 (1939) 178.
9 C. W. Davies, *Ion Association*, Butterworth, Washington, 1962, p. 96.
10 S. Winstein and H. J. Lucas, *J. Am. Chem. Soc.*, 60 (1938) 836.
11 R. M. Keefer, L. J. Andrews and R. E. Kepner, *J. Am. Chem. Soc.*, 71 (1949) 3906.

REVIEW

GLOW-DISCHARGE ELECTROLYSIS

A. HICKLING AND M. D. INGRAM

Donnan Laboratories, Liverpool University, Liverpool (England)

(Received April 1st 1964)

INTRODUCTION

If an electric discharge is passed to a conducting solution from an electrode situated in the gas space above the surface, remarkable chemical reactions can be brought about in the liquid phase and the process is referred to as glow-discharge electrolysis (GDE). It differs fundamentally from processes involving electric discharges between metallic electrodes in gases since in GDE the solution itself is one of the electrodes and the reactions of interest are those which occur within the liquid phase. In the usual experimental arrangement, the electrode above the surface is the anode while the cathode is immersed in the electrolyte; once the discharge has been started, it can be maintained at voltages of 500 V upwards with the gas or vapour at reduced pressure and substantial currents can be passed to the liquid surface. The technique first attracted attention as a method of carrying out electrolysis without a solid electrode in contact with the electrolyte solution, but it was soon realised that the chemical effects produced were far in excess quantitatively of those predicted by Faraday's Laws. Recent work has shown that charge transfer is only a minor factor in GDE, and current views consider that the chemical effects are produced by charged particles which are accelerated in the potential fall near the electrolyte surface and enter the liquid with energies which may be of the order of 100 eV. These can dissociate or excite solvent molecules by collision, in addition to entering into charge–transfer reactions, and the chemical effects are analogous to those produced by ionising radiations particularly low energy alpha particles. It is found that quantity of electricity is still the most important variable in determining the amount of chemical change brought about, since it governs the total number of charged particles entering the liquid phase, but we now have a new type of electrolysis arising from energy transfer in addition to the charge transfer of conventional electrochemistry.

HISTORY

The earliest observations on GDE were those of GUBKIN[1] (1887) who effected reduction of metallic salt solutions using a glow-discharge cathode, and KLÜPFEL[2] (1905) who liberated iodine from potassium iodide electrolytes using a glow-discharge anode. MAKOWETSKY[3] (1911) showed that in the GDE of dilute sulphuric acid solutions, hydrogen peroxide was one of the main products in solution; the yield was greater than 1 equiv./F but when the amounts of hydrogen and oxygen evolved were taken into account an overall oxidation balance was maintained. KLEMENC and co-workers[4] (1914–1954) in an extensive series of papers studied a wide range of aqueous electrolytes including sulphuric acid solutions, halides and oxy-halogen salts, oxidisable substances such as ferrous and stannous salt solutions, and some organic substrates. The conditions employed frequently led to results of a complex nature, but it was clearly established that in general two types of reaction occurred which were distinguished as *polar* and *apolar* reactions respectively. The first corresponded to the normal charge-transfer reaction to be expected on electrolysis, but the latter, which often predominated, corresponded in general to oxidation accompanied by evolution of hydrogen from the solution. KLEMENC's final view as to the mechanism of GDE was that the apolar reaction arose from the formation of OH radicals in the cathode fall in the discharge; these dissolved in the surface of the solution and reacted with the oxidisable species present. Recent fundamental investigations by HICKLING and associates[5] (1950–1964) have concentrated on the study of very simple systems. These seem to show that the reactions originate in the liquid phase and closely resemble those brought about by ionising radiations. Initial decomposition of solvent molecules is considered to be followed by interaction of the radicals produced in competition with the scavenging action of reactive species in solution, and many of the concepts of radiation chemistry can be applied to the situation. Miscellaneous papers[6] on particular aspects and applications of GDE are fairly numerous, and a somewhat similar process—that of spark electrolysis at atmospheric pressure—has been studied particularly by DE BECO[7].

EXPERIMENTAL TECHNIQUE

The experimental cell can take many forms; two convenient types are shown in Fig. 1. Where it is desirable to prevent products produced in the glow-discharge from being reduced at the cathode, an H-cell may be used with anode and cathode compartments separated by a sintered-glass diaphragm; otherwise a one-compartment cell with the cathode immersed directly in the solution may be employed. The cell is closed by ground-glass or rubber stoppers carrying the cell components. The anode may be a platinum wire attached to a tungsten rod sealed into a glass holder; the nature of the

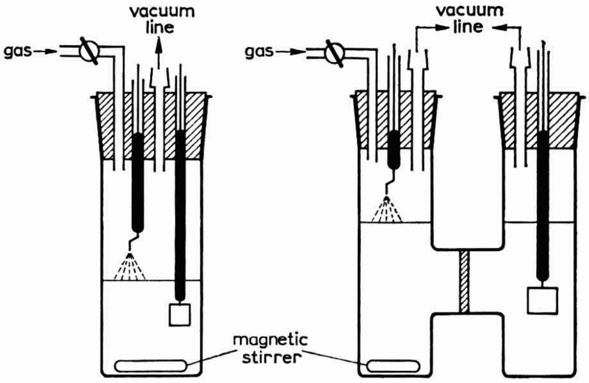


Fig. 1. Cells for glow-discharge electrolysis.

cathode is not usually important but on a small scale a platinum-foil electrode is convenient. It is often useful to have the anolyte stirred and this can be done by a magnetic stirrer. Considerable heat is dissipated in the discharge and the cell is therefore almost completely immersed in a suitable coolant bath; for GDE with aqueous solutions, circulated tap water is adequate. Where the solvent is particularly volatile it is advantageous to have a reflux condenser in the exit from the anode compartment. The anode and cathode compartments are connected to a vacuum line in which a constant pressure in the range 25–250 mm can be maintained by a float manostat. Where it is desired to control the gaseous atmosphere in the discharge, provision is made for admitting a slow stream of gas through the cell during electrolysis; this is also desirable with aqueous electrolytes to prevent any explosion risk due to accumulation of hydrogen and oxygen in the system.

Current is best supplied from a rectifier of adjustable voltage (0–1500 V) through an ammeter, hydrogen–oxygen coulometer of the Lingane type, and a suitable ballast resistor. The last is necessary to maintain the discharge stable and should give a voltage drop of 100–200 V; resistors of 1000–10,000 Ω according to the current being passed are suitable. To start the discharge, a pulse from an induction coil or high voltage transformer can be used, or the anode may be touched momentarily to the liquid surface. Once initiated, the discharge is very steady and currents in the range 0.02–0.2 A can readily be used with the anode at distances of up to 1 cm from the surface; voltage across the cell varies with the anode-to-liquid distance and with the resistance of the solution but is usually in the range 500–800 V, and the major part of this voltage drop (about 400 V) occurs very close to the liquid surface.

If the electrode above the surface is made a cathode instead of an anode, most of the voltage drop occurs near it and there is only a relatively small anode fall near the liquid surface. The chemical effects produced in the solution with this arrangement are small and the metal electrode becomes white hot and may melt. If it is desired to operate a glow-discharge cathode in this way, it is necessary to have a massive metal electrode above the surface and a platinum cone with the point towards the liquid can be used. Alternating current can be used for GDE, but most of the chemical reaction produced occur during the half cycles in which the electrode above the surface is positive.

A method has recently been worked out[8] of effecting GDE at atmospheric pressure with very simple apparatus. In this method, which is termed contact glow-discharge electrolysis (CGDE), the anode is a thin wire which is immersed in the electrolyte. On passing a small current, conventional electrolysis occurs, but if the current is progressively increased, a point is reached at which the electric power dissipated near the electrode surface is sufficient to vaporise the solvent locally. The anode then becomes enveloped in a sheath of vapour through which GDE occurs. The chemical effects produced are similar to those obtained with the more usual arrangement, but the discharge is automatically initiated and maintained and the overall voltage necessary may be as low as 500 V.

DISCHARGE CHARACTERISTICS

With a wire anode above the solution surface, the discharge appears as a sharply defined cone between the tip of the anode and a circular glow-spot in the electrolyte surface; occasionally the glow-spot appears as a slowly rotating clover-leaf pattern.

If a disc or plate anode is used, the discharge will normally emanate from one point although this may wander over the anode surface. The colour of the discharge depends upon the nature of the vapour present; with aqueous electrolytes in air it is pink-blue, and with solutions in liquid ammonia it is yellow-green.

The area of the glow-spot varies with experimental conditions tending to rise with increase in current and with anode-to-solution distance, and to decrease with rise in pressure; it seems to be largely independent of the nature and concentration of the electrolyte and the temperature. The current density (CD) of the discharge at the liquid surface is an important parameter; it is usually taken to be the current passing divided by the area of the glow-spot. At a given pressure and electrode distance, the CD is substantially independent of the current passing, over a considerable range; any change is in fact in the direction of a slight decrease in CD with increase of current. Increase of electrode–solution distance also decreases the CD but again the effect is relatively small. The largest variation in CD is produced by change of pressure, and for aqueous solutions under the usual conditions employed the relation $I/p = 0.03$ holds fairly well where I is the CD in A cm^{-2} and p is the pressure in cm of mercury. Thus over the range 50–250 mm pressure the CD can be varied from 0.15–0.75 A cm^{-2}. With solutions in liquid ammonia the CD values are of the same general order of magnitude.

The distribution of potential within the discharge has been investigated using a horizontal platinum-wire probe-electrode and measuring with a valve voltmeter its potential relative to the liquid at various distances from the surface. This reveals a state of affairs similar to that found in discharge between metallic electrodes in a gas at reduced pressure. The major potential drop occurs in the cathode fall near to the liquid surface, and this is independent of nearly all experimental variables. Thus in Fig. 2 are shown the probe voltages in the GDE of an aqueous electrolyte at various pressures. It was not practicable to have the probe nearer the surface than 1 mm, but it can be seen that the three curves intersect at a distance of about 0.05 cm from the surface and that the voltage here is about 415 V. This value was found to be substantially constant, independent of current, electrode distance, pressure, gaseous at-

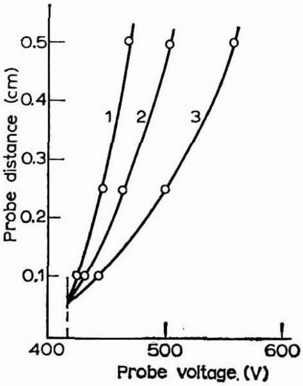


Fig. 2. Measurement of potential drop near liquid surface at pressures: (1), 27; (2), 50; (3), 100 mm mercury.

mosphere, and nature and concentration of the electrolyte. It presumably represents the cathode fall for a discharge through water vapour to a liquid water cathode. The total voltage across the discharge contains also the fall of potential in the positive column, which depends upon its length and upon the pressure, and the anode fall near the electrode above the surface. These contributions are much smaller than the cathode fall and apparently play little or no part in the production of chemical reactions in the *liquid* phase. Thus the cathode fall of 415 V is a minimum voltage to which the total applied voltage tends at very small anode–liquid distances, and it is noteworthy that in the technique of CGDE the minimum value for glow-discharge has been found to be closely similar at 410 V. It would be expected that changing the nature of the liquid would affect the cathode fall, and with liquid ammonia as solvent the observed value is 390 V; again it is independent of most experimental variables and occurs within about the same distance of the solution surface.

When the electrode above the liquid is made a cathode the nature of the discharge is changed completely. The cathode fall now occurs close to the metal electrode, which becomes very hot, and the cathode glow spreads over its surface. The discharge to the solution appears as a narrow cylindrical pencil of light and the glow-spot in the liquid surface is very small, usually about 2–3 mm in diameter, leading to a very high CD of about 1 A cm^{-2}. The fall of potential near the liquid is now the anode fall in the discharge and is about 30 V. When 50-cycle alternating current is used for GDE the discharge is not continuous but stops and restarts twice in each cycle with an appreciable gap between the successive anodic and cathodic pulses each of which exhibits its normal DC features.

CHEMICAL RESULTS OF GLOW-DISCHARGE ELECTROLYSIS

Water

When aqueous solutions of inert electrolytes are subjected to GDE the products arise from the decomposition of water and consist of hydrogen, oxygen, and hydrogen peroxide. Hydrogen peroxide is initially formed in an amount proportional to the quantity of electricity passed, but the yield is higher than would be expected electrolytically; the excess oxidation over that possible by charge transfer is balanced by an equivalent amount of hydrogen liberated into the gas phase, As the hydrogen peroxide accumulates in the solution, a decomposition reaction due to the glow-discharge sets in and, ultimately, a stationary concentration is reached when it is decomposing as fast as it is formed.

The amount of hydrogen peroxide produced by a given quantity of electricity is largely independent of the current used and of factors affecting the discharge such as the electrode distance, the power dissipated, the shape and size of the electrode, the pressure, and the nature of the gaseous atmosphere, indicating that it probably arises by a reaction in the liquid rather than in the gaseous phase. In considering the results of GDE quantitatively, the yield is usually expressed in equivalents or moles per faraday (equiv./F or mole/F) and it is convenient to distinguish between the integral and differential yield. The integral yield represents the amount of substance formed or consumed for the passage of a given quantity of electricity. The differential yield expresses the instantaneous rate of the process in equiv./F or mole/F at a particular point in electrolysis when the concentrations of substances in the solution can be specified. This differential yield will be denoted by G and it is particularly significant at the start of GDE. It is analogous in some ways to the quantity used in radiation chemistry where the yield is expressed in molecules/100 eV, but it should be emphasised that as used here it is a yield for a given quantity of electricity and this will only be proportional to the electrical energy put in if a constant voltage term is involved. The initial *G*-value for production of hydrogen peroxide varies from about 1.1 equiv./F in 0.05 *M* sulphuric acid to 1.8 equiv./F in 0.05 *M* sodium bicarbonate solution; in strongly alkaline solutions no hydrogen peroxide can be detected, probably owing to its ready anodic decomposition by discharge of the HO_2^- ion. With any given electrolyte, *G* increases with increasing electrolyte concentration up to a limiting value, and it is also favoured to some extent by factors tending to increase CD in the glow-spot, such as rise of pressure. As hydrogen peroxide accumulates in the anolyte, *G* decreases and ultimately approaches zero, the integral yield then tending to a limiting value. This behaviour is due to a decomposition reaction which hydrogen peroxide itself undergoes on GDE; this reaction can be studied by carrying out GDE with hydrogen peroxide solutions of higher concentration when negative *G*-values are observed. Variation of the integral yield of hydrogen peroxide with quantity of electricity passed, and variation of the differential yield of hydrogen peroxide with concentration are illustrated in Fig. 3 for 0.04 *N* sulphuric acid as anolyte.

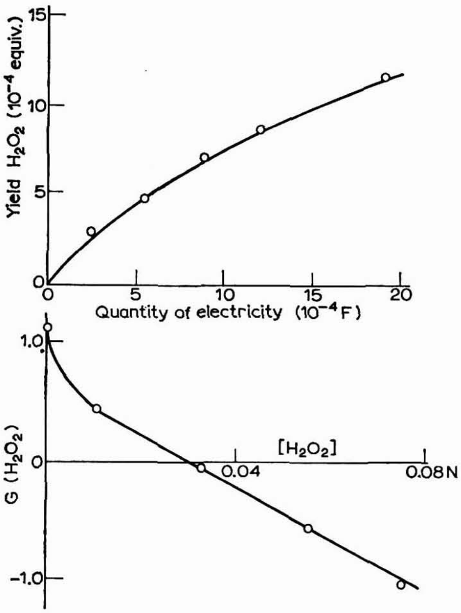


Fig. 3. Integral and differential yields of hydrogen peroxide.

Assuming that the rate of formation of hydrogen peroxide is proportional to the current and its decomposition is dependent both on the current and upon its concentration, we may write

$$\frac{d(H_2O_2)}{dt} = G_0 \frac{I}{F} - G_0 \frac{I}{F} k \, [H_2O_2]$$

where (H_2O_2) is the integral yield; G_0, the initial differential yield; I, the current; and k, a coefficient for the decomposition reaction. On integration and application of the condition that there is no hydrogen peroxide present at the start of electrolysis, the equation becomes

$$(H_2O_2) = \frac{V}{k}(1 - e^{-G_0kq/V})$$

where q is the quantity of electricity and V the volume of the solution. This equation fits the experimental results very closely[9]. The stationary concentration of hydrogen peroxide which can be achieved by GDE in sulphuric acid varies from about 0.03 N at 50 mm to 0.12 N at 760 mm pressure.

Although the formation of hydrogen peroxide is not substantially dependent upon the nature of the gas present above the electrolyte, the yields tend to be somewhat higher with air or oxygen than with nitrogen, and to be slightly lower if hydrogen is used. The presence of chloride ions in the electrolyte seems unfavourable to hydrogen peroxide production, and the presence of 0.02 M NaCl in the sulphuric acid completely inhibited its formation although the chloride ion was not itself appreciably consumed.

Spark electrolyses of solutions of inert electrolytes furnishes very similar yields of hydrogen peroxide to those obtained in GDE and the effects of alkalinity, chloride ion, and gas atmosphere are closely parallel[7].

Aqueous solutions of oxidisable substrates

The anodic GDE of oxidisable substances in water such as ferrous, stannous, and cerous salts, potassium ferrocyanide, and sodium azide, brings about considerable oxidation, and yields as high as 7 equiv./F can be realised. In dilute solutions there is usually hydrogen peroxide formation as well as oxidation of the substrate; with increase in substrate concentration, peroxide formation diminishes and the oxidation yield increases towards a limiting value. The results are best displayed by plots of G (oxidation) and G (H_2O_2) against concentration of substrate, and in Fig. 4, typical graphs for ferrous, cerous, azide and ferrocyanide ions are shown. In general it is seen that the differential oxidation yield increases with increasing concentration and approaches a limiting value asymptotically; the ferrocyanide case is abnormal here in that, over a substantial range of concentrations, the yield is accurately proportional to the concentration, and the limiting value is attained abruptly when the concentration is 0.125 M. The behaviour at low concentrations depends on the reaction of the substrate or its oxidation product, with hydrogen peroxide. Where the substrate is readily oxidised by hydrogen peroxide, as is the case with ferrous sulphate, there is a finite oxidation yield even as the substrate concentration tends to zero. On the other hand, where the oxidation product can be reduced by hydrogen peroxide, as for example with ceric sulphate, a certain minimum concentration of substrate is necessary for any net oxidation to occur. It should be noted that with ferrocyanide even at the highest concentrations there is still a finite yield of hydrogen peroxide. From Fig. 4 it is seen that at the highest ferrous ion concentrations, G (oxidation) tends to a limiting value in the region of 7 equiv./F, and about the same limit is reached with azide ions; with ferrocyanide ions it is about 5.7 and with cerous ions just over 5 equiv./F.

The above results refer to GDE in an inert atmosphere of nitrogen. Working with oxygen-saturated solutions of ferrous sulphate the limiting *G*-value is notably increased to about 12.5 equiv./F, but with the other substrates the presence of oxygen has little effect. In the formation of hydrogen peroxide in inert electrolytes a salt effect has been noted whereby the yield is increased by raising the electrolyte concentration. Where the substrate is oxidised by hydrogen peroxide, as in the ferrous case, a similar rise in oxidation yield occurs, but where the substrate is fairly stable to hydrogen peroxide, as with ferrocyanide and azide, little salt effect is apparent. With cerous sulphate, where the oxidation product is reduced by hydrogen peroxide, the addition of sodium sulphate to the medium decreases the oxidation yield. It has been mentioned that chloride ion can inhibit the formation of hydrogen peroxide and it is also found to decrease the oxidation yields appreciably except with ferrocyanide where the production of ferricyanide is scarcely affected. In general increase of CD in the glow-spot, *e.g.*, by rise of pressure, is unfavourable to oxidation of substrate unless this is itself oxidised by hydrogen peroxide, when there is very little change.

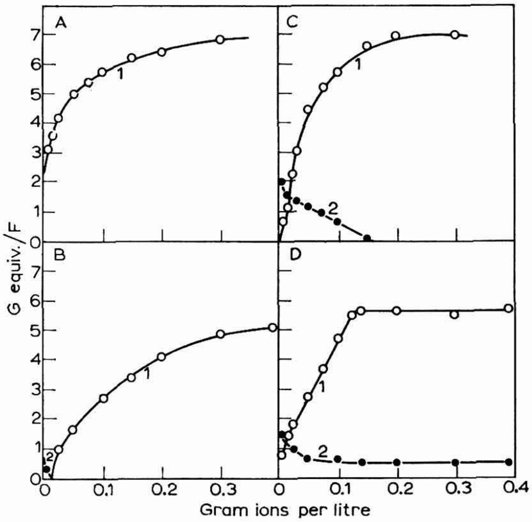


Fig. 4. Oxidation of various substrates: (1), *G* (oxidation); (2), *G* (H_2O_2). A, ferrous ion; B, cerous ion; C, azide ion; D, ferrocyanide ion.

Other reactions in water

With sulphuric acid solutions of concentration greater than 1 *M*, GDE produces persulphuric acid, $H_2S_2O_8$, and permonosulphuric acid, H_2SO_5, in addition to hydrogen peroxide[4]; the yields are increased by the addition of potassium fluoride, and diminished in the presence of hydrochloric acid. GDE of solutions of halides and oxy-halogen salts yields very complex results; some liberation of halogen may occur, and with iodides this can predominate, but both formation and reduction of oxy-halogen salts frequently takes place and the net process after a short time is often liberation of oxygen. It seems likely that in some cases a chain reaction may be involved; thus in the electrolysis of sodium chlorite solution a yield of 34 equiv. of oxygen/F has been reported[4]. GDE of aqueous solutions of organic compounds has not so far been very thoroughly investigated, but observations with ethanol, formic and acetic acids show that there is general oxidation accompanied by the evolution of hydrogen and sometimes the formation of hydrocarbons[4]. BROWN, WILHIDE AND ELMORE[6] have reported that GDE of a solution of formamide in dilute sulphuric acid will produce oxamide, $(CONH_2)_2$, a reaction which they attribute to free OH-radicals. GDE of an aqueous solution of acrylonitrile will readily bring about polymerisation, and this has been suggested[10] as a general method for initiating polymerisation of monomers present either in solution or in emulsion form.

Non-aqueous reactions

HICKLING AND NEWNS[5] have found that with liquid ammonia as a solvent and solutes such as ammonium nitrate, GDE produces hydrazine as the main product in solution. The initial G (N_2H_4) yield is about 2.5 moles/F and this falls off slowly as hydrazine accumulates in the liquid, but stationary concentrations as high as 2 M can be reached. Anhydrous hydrazine can be readily isolated from the resulting solution by distillation, and GDE has been suggested as a useful route for the synthesis of this substance[11]. Anodic GDE in liquid ammonia shows many features similar to those observed in aqueous solutions. The cathode fall of 390 V is only slightly less than with water, the main product, hydrazine, is analogous to hydrogen peroxide; its formation is again largely independent of conditions in the discharge on the vapour side of the interface, and hydrazine itself like hydrogen peroxide is ultimately decomposed by GDE when its concentration is sufficiently high. It is apparent that there is a general pattern of reaction beginning to emerge.

So far, work on GDE in other non-aqueous systems is limited to the observations of CADY, EMELEUS AND TITTLE[6] using liquid sulphur dioxide with small amounts of water present to render it conducting. With both a glow-discharge anode and cathode, sulphuric acid and sulphur were produced as the main final products; the yield of sulphuric acid was greater with a glow-discharge anode and amounted to about 14 moles/F, while about 5 g atom/F of sulphur was formed in both cases.

Cathodic GDE

As already mentioned, glow-discharge with a cathode above the surface is far less productive of chemical reaction than when the more usual anodic arrangement is employed. It might at first sight be thought that cathodic GDE would produce chemical reduction in the liquid phas since it corresponds to the introduction of electrons. THON[6] found that solutions of salts of silver, gold, and platinum could in fact be reduced to the metallic state, but in general, with other metallic salts only a precipitate of the hydroxide of the metal could be formed in the glow-spot. More recently[12] a full investigation of cathodic GDE has shown that the reactions produced are generally of the same type as in anodic GDE but on a much diminished scale, and any reductions which occur seem to be due to hydrogen peroxide. Thus with dilute sulphuric acid even in a hydrogen atmosphere a small yield of hydrogen peroxide is obtained with a G (H_2O_2) value of 0.04 equiv./F; with a ferrous sulphate electrolyte, oxidation occurs with a limiting value at high ferrous concentrations of 0.28 equiv./F. Both these values are markedly increased in the presence of oxygen to 0.15 and 1.9 equiv./F respectively. On the other hand using solutions of ferric salts no certain reduction has been established; some reduction does occur with ceric, dichromate, and ferricyanide solutions but this may be due in part to hydrogen peroxide. The general conclusion seems unavoidable that in cathodic GDE the reactions are qualitatively similar to those in anodic GDE, but that the effects are much smaller because there is only a small potential drop at the liquid surface.

THE MECHANISM OF GLOW-DISCHARGE ELECTROLYSIS

It now seems possible to make an approach at constructing an integrated picture of the processes giving rise to the characteristic features of GDE. From the experimental results the following general conclusions seem to emerge.

1. The products of GDE seem largely independent both qualitatively and quantitatively of conditions existing in the gas or vapour phase. Thus the amount of dissipated power, which can be varied widely by change of current or electrode–solution distance, is without effect nor does the nature of the gas present affect the results substantially. Furthermore, experiments have been carried out seeking to imitate the results of GDE by passing a discharge between metallic electrodes just above the liquid surface, but they have all been unsuccessful. Thus the indication is that the chemical reactions arise primarily in the liquid phase.

2. The initiation of chemical reaction seems to be bound up with the fall of potential near the liquid surface and this is independent of most experimental variables. Quantity of electricity passed is the chief factor controlling the yields, and this strongly suggests that it is the amount of electrical energy put into the system due to the field near the surface which determines the kind and amount of chemical reaction.

3. The chemical reactions produced in GDE are analogous to those which arise by the action of ionising radiations on the liquids concerned, and the similarity is particularly striking if the effects of alpha particles are considered. These radiation processes are usually interpreted by reactions of radicals arising from the break-up of solvent molecules, and similar mechanisms involving OH and NH_2 radicals will account plausibly for many of the GDE reactions in aqueous and ammoniacal solutions.

It seems somewhat improbable that electrons can be emitted directly from the surface of a liquid electrolyte (although this was in fact suggested by BRAUNBEK[6]), and if this is so it follows that in experiments with a glow-discharge anode the current must be conveyed by positive gaseous ions which are driven into the liquid from the gas phase and subsequently discharged. The fact that the nature of the gas present has usually little influence on the process, suggests that the discharge may well pass ultimately through solvent vapour in all cases and this is not unlikely since the local temperature under the glow-spot must be relatively high. With aqueous solutions we shall thus have the ions present in ionised water vapour; we have no certain knowledge what these will be at the pressures used in GDE, but observations made with the mass spectrometer at much lower pressures[13] have shown that the main positive ion present is H_2O^+, and for simplicity this will be assumed to be the species carrying the charge across the interface. These ions will be accelerated in the cathode fall near the liquid surface and will enter the liquid with considerable energies. The maximum energy which they could have would be 415 eV if they passed through the cathode fall without any loss of energy. In practice, of course, much of this energy will be dissipated in collisions in the vapour phase and the average energy will depend on the mean free path of the ions in the discharge. Attempts to calculate this have not, so far, led to meaningful results. If the cathode fall is taken as 415 V extending uniformly over 0.05 cm, and the temperature is taken as the boiling point of the solution, then at 50 mm pressure a value of about 4 eV for the energy is obtained, but this is certainly much too low, and the experiments of CHAUDRHI AND OLIPHANT[14] have shown that the energies of ions passing through a cathode fall can be much greater than the values obtained by calculations of this kind. What seems clear is that the gaseous ions may well enter the liquid with energies adequate to bring about dissociation of water molecules, and comparison with radiation chemistry suggests that an average energy of *ca.* 100 eV is a plausible value.

The penetration of these ions into the liquid phase will be very small. Comparison with slow alpha particles[15] suggests that a linear energy transfer value of at least 10 eV/Å would be probable, and this would imply a range of only some 10 Å. A very rough idea of the range may also be obtained by treating the ions as neutral particles slowed down by the viscous drag of the liquid as given by Stokes' Law, and this leads also to an order of magnitude of 10 Å. Thus the primary reaction zone will be a very thin disc in the surface of the solution of area *ca.* 0.5 cm^2 and thickness perhaps 10 Å. Within this primary reaction zone the bombarding ions will each ionise or activate several water molecules by collision, and one water molecule per ion will be broken up by charge transfer, thus:

collision

$$\text{ionisation} \qquad H_2O \rightsquigarrow \begin{array}{ccl} H_2O^+ & \overset{H_2O}{\rightarrow} & OH + H_3O^+ \\ + & & \\ e & \overset{H_2O}{\rightarrow} & H + OH^- \end{array} \qquad \text{(a)}$$

$$\text{activation} \qquad H_2O^* \rightsquigarrow OH + H \qquad \text{(b)}$$

charge transfer

$$H_2O^+ + H_2O \rightarrow OH + H_3O^+ \qquad \text{(c)}$$

The ultimate result in all cases is the production of free OH-radicals and sometimes H atoms. However, because the excited species are packed so closely together there is a good chance that the precursors of the free radicals may interact thus:

$$2\ H_2O^+ \rightarrow H_2O_2 + 2\ H^+ \qquad \text{(d)}$$

$$2\ H_2O^* \rightarrow H_2O_2 + H_2 \qquad \text{(e)}$$

giving a molecular yield of H_2O_2 and H_2, and of course geminate recombination between precursors or free radicals may reform water molecules. Thus a mixture of OH, H, H_2O_2 and H_2 will be diffusing out of the primary zone, the relative amounts being governed by spatial considerations. As these diffuse into the body of the solution we shall have a secondary reaction zone in which they may interact with one another or be scavenged by reactants in the solution. The situation is diagrammatically represented in Fig. 5. In some ways the primary reaction zone may be likened to a spur in radiation chemistry; within the disc, conditions will not be uniform but will consist of many separate hot spots of activity around each incoming ion, but as the radicals and molecular products diffuse away from their initial positions they will merge into a single downward drift into the solution and in this sense the reaction zone may be considered as a single spur which is located in a fixed position and constantly renewed.

As the radicals and products diffuse into the body of the electrolyte they will interact among themselves and with any reactive substrate in the solution. The main reactions which seem to be of importance in GDE are as follows:

interaction of radicals and products

$$H + OH \rightarrow H_2O \qquad (f)$$

$$OH + OH \rightarrow H_2O_2 \qquad (g)$$

$$H + H \rightarrow H_2 \qquad (h)$$

$$\left.\begin{array}{ll} & OH + H_2O_2 \rightarrow H_2O + HO_2 \\ \text{followed by} & OH + HO_2 \rightarrow H_2O + O_2 \end{array}\right\} \qquad (i)$$

interaction with substrate

$$\left.\begin{array}{ll} & OH + S \rightarrow S^+ + OH^- \\ \text{or} & OH + SH \rightarrow S + H_2O \end{array}\right\} \qquad (j)$$

$H_2O_2 \rightarrow$ possible oxidation and reduction reactions with substrate and its oxidation products. (k)

On this basis many of the features of GDE can be understood qualitatively and in part quantitatively. Thus in aqueous solutions of inert electrolytes the chief product in solution will be hydrogen peroxide, arising partly in the primary zone by reactions (d) and (e), and in the secondary zone by reaction (g). As it accumulates in the solution, reaction (i) will increase in speed until ultimately, at a certain hydrogen peroxide concentration, it will be decomposed as fast as it is formed. Alternatively, starting with a more concentrated hydrogen peroxide solution, it will be decomposed on GDE by reaction (i) until the stationary state is again reached. Increase of CD would be expected to favour production of hydrogen peroxide by reactions (d), (e) and (g), and hence increase its yield and also the stationary concentration. This is in general conformity with what is found, *e.g.*, for the effect of pressure; in some recent work[16]

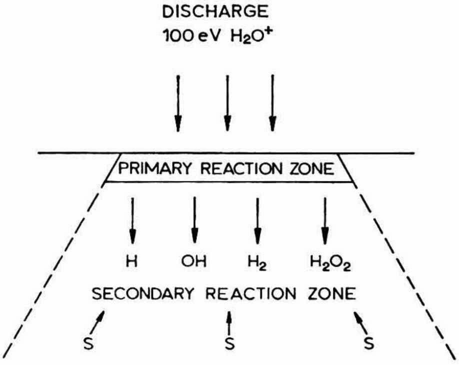


Fig. 5. Reaction zones.

very high CD values have been achieved by the use of a condensed glow-discharge. Here a condenser charged to a high voltage is periodically discharged between the anode and the surface of the solution; each discharge is of very short duration but corresponds to a momentary very high CD. Using this technique with a dilute sulphuric acid electrolyte, G (H_2O_2) was found to be increased from 1.1 to 2.0 equiv./F and the stationary concentration from 0.03 to 0.11 N under otherwise identical conditions. In so far as some of the hydrogen peroxide arises from reaction (d), increase in salt concentration would be expected to increase the yield, as is again found in practice. The effect of chloride ion in reducing the yield of hydrogen peroxide is probably due to its removal of OH-radicals, *e.g.* by the reaction

$$\left.\begin{array}{rl} & Cl^- + OH \rightarrow Cl + OH^- \\ \text{followed by} & Cl + H \rightarrow Cl^- + H^+ \end{array}\right\} \qquad (l)$$
$$\text{or} \quad Cl + OH \rightarrow HOCl$$

and subsequent decomposition. The rise in yield of hydrogen peroxide in oxygenated solutions is probably due to reduction of oxygen by hydrogen atoms to HO_2 radicals and their subsequent interaction

$$\left.\begin{array}{l} H + O_2 \rightarrow HO_2 \\ 2\,HO_2 \rightarrow H_2O_2 + O_2 \end{array}\right\} \qquad (m)$$

When an oxidisable substrate is present it will react with the radicals and products present in the secondary reaction zone and may in some cases be able to penetrate into the primary zone and react with precursors of the radicals, although this is probably exceptional. With ferrous ions, which can be oxidised by OH, H_2O_2, and HO_2, one would expect G (oxidation) to increase with increasing ferrous ion concentration as reactions (j) and (k) become increasingly effective competitors with reactions (f), (g), (h) and (i), and the limiting oxidation yield at very high ferrous ion concentrations should measure the sum of the OH and H_2O_2 emerging from the primary reaction zone. Under the conditions normally used this is about 7 equiv./F. In the presence of oxygen the formation of HO_2 radicals from H atoms would be expected to increase the oxidation yield, as is observed. With other oxidisable substrates a similar state of affairs will exist, but where they are not oxidised by hydrogen peroxide the yield will be lower, and indeed if the oxidation product is reduced by hydrogen peroxide, as are ceric salts, the yield will be lower still. Whether the presence of oxygen has any effect will depend upon whether the substance can be oxidised by HO_2 radicals. The abnormal features shown by ferrocyanide might be explained by suggesting that in virtue of its high negative charge the $Fe(CN)_6{}^{4-}$ ion can act as a scavenger within the primary reaction zone for H_2O^+ ions which may be precursors of the OH radicals produced by dissociation of water molecules. On this basis the probability of a H_2O^+ ion reacting before decomposing would be directly proportional to the ferrocyanide concentration, and at a particular concentration all the H_2O^+ ions might react within their average life period. It is noteworthy that in the ferrocyanide case there is a finite yield of about 0.5 equiv./F of hydrogen peroxide even at the highest substrate concentrations, and the limiting G (oxidation) for ferrocyanide is about 5.7. If these values are taken to represent the molecular yield of hydrogen peroxide from the primary zone and the yield of OH radicals or their precursors, respectively, the limiting oxidation yields in other cases can be calculated according to the reaction of the substrate or its oxidation product with hydrogen peroxide. Thus with ferrous and azide ions the limiting G (oxidation) would be 6.2, and with cerous ions 5.2; the experimental results do not coincide precisely with these but the general pattern is followed.

The above discussion has referred to limiting oxidation yields when the substrate concentration is high enough for the oxidising species to be scavenged completely. At concentrations lower than this, the yields will be governed by the competition of the reactions (f), (g), (h), (i) (j), and (k) under the circumstances of experiment. If we suppose that a constant yield of n equiv./F of OH emerges from the primary zone, and that the velocities of the competing reactions are v_f, v_g, ... etc., then (neglecting the molecular yield of hydrogen peroxide which is usually small) G-values can be written down as follows:

$$\begin{array}{lll} \text{inert electrolytes} & G\,(\mathrm{H_2O_2}) & = n(v_g - v_i)/(v_f + v_g + v_i) \\ \text{ferrous ion} & G\,(\text{oxidation}) & = n(v_j + v_g)/(v_f + v_g + v_j) \\ \text{cerous ion} & G\,(\text{oxidation}) & = n(v_j - v_g)/(v_f + v_g + v_j) \end{array}$$

assuming that hydrogen peroxide reacts quickly and completely with ferrous and ceric ions in the last two cases. The velocity terms will involve, of course, the concentrations of the radicals in the secondary reaction zone, and these will vary as they advance into the solution. Thus we have a very complex problem in kinetics, analogous in some ways to the mixing of reactants in flow-systems, which would require for its solution a complete knowledge of the concentration profiles of all the reacting species in the zone. This problem has not yet been solved, but the results of some very crude approximations are not without interest. The velocity, v_j, of reaction with substrate must involve the substrate concentration and thus in the ferrous case, for example, the given expression may be re-written

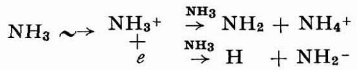
$$G\,(\text{oxidation}) = n([\mathrm{Fe^{2+}}] + A)/([\mathrm{Fe^{2+}}] + A + B)$$

The quantities A and B will depend upon the concentrations of the reactive radicals and cannot therefore be independent of $[\mathrm{Fe^{2+}}]$, but over a limited range of substrate concentrations this type of expression has been found[5] to fit experimental results fairly closely if A and B are given empirical values and n is about 7. If the equations for $G\,(\mathrm{H_2O_2})$ and G (oxidation) for ferrous ion are compared, it is seen that at very low ferrous ion concentrations when $v_j \rightarrow 0$, the limiting oxidation yield should approximate to the hydrogen peroxide yield under conditions such that v_i is very small. Thus G (oxidation) $[\mathrm{Fe^{2+}}] \rightarrow 0$ should give an upper limit to $G\,(\mathrm{H_2O_2})$ in inert electrolytes. The limiting oxidation yield is in fact 2.5 equiv./F and $G\,(\mathrm{H_2O_2})$ yields up to about 2 equiv./F have been observed in practice.

GDE in liquid ammonia can be interpreted very similarly to that in aqueous solutions with the amino radical, $\mathrm{NH_2}$, as the main reactive entity in place of the OH-radical. In the primary reaction zone the analogous reactions will be:

collision

ionisation



$$\mathrm{NH_3} \rightsquigarrow \begin{array}{c} \mathrm{NH_3^+} \\ + \\ e \end{array} \begin{array}{l} \xrightarrow{\mathrm{NH_3}} \mathrm{NH_2} + \mathrm{NH_4^+} \\ \xrightarrow{\mathrm{NH_3}} \mathrm{H} + \mathrm{NH_2^-} \end{array} \qquad \text{(n)}$$

activation $\mathrm{NH_3^*} \rightsquigarrow \mathrm{NH_2} + \mathrm{H}$ (o) *charge transfer*

$$NH_3^+ + NH_3 \rightarrow NH_2 + NH_4^+ \qquad (p)$$

A molecular yield of hydrazine may result from interaction of precursors of NH_2, thus:

$$2\ NH_3^+ \rightarrow N_2H_4 + 2\ H^+ \qquad (q)$$

$$2\ NH_3^* \rightarrow N_2H_4 + H_2 \qquad (r)$$

and diffusing out of the primary zone will be a mixture of NH_2, H, N_2H_4 and H_2. Interaction between these can lead to reformation of ammonia

$$NH_2 + H \rightarrow NH_3 \qquad (s)$$

dimerisation to hydrazine and to hydrogen

$$NH_2 + NH_2 \rightarrow N_2H_4 \qquad (t)$$

$$H + H \rightarrow H_2 \qquad (u)$$

and decomposition of hydrazine by NH_2-radicals

$$\left.\begin{array}{ll} & NH_2 + N_2H_4 \rightarrow N_2H_3 + NH_3 \\ \text{followed by} & N_2H_3 + NH_2 \rightarrow N_2 + H_2 + NH_3 \end{array}\right\} \qquad (v)$$

The formation of hydrazine and its build-up to a stationary concentration follows on this scheme, and the experimental values suggest that about 12 equiv. NH_2/F are probably produced.

GLOW-DISCHARGE ELECTROLYSIS AND RADIATION CHEMISTRY

Whatever its detailed mechanism may be, GDE is undoubtedly a form of electrolysis in which some of the electrical energy put into the system initiates decomposition of solvent molecules by a process additional to ordinary charge transfer, and it are the reactions of the radicals resulting which determine the chemical changes brought about. An attempt has been made here to develop a consistent picture of the process in terms of gaseous ions accelerated in a constant cathode fall communicating their energy to solvent molecules in the liquid state, and this permits the fruitful use of many of the concepts and ideas developed in radiation chemistry. Other explanations are, however, possible. It could be suggested that solvent *vapour* is dissociated in the the cathode fall and that the radicals produced then disolve in the liquid and bring about reaction. This view was latterly held by KLEMENC[4] and it is impossible to exclude it, but it does not seem to fit the experimental facts so closely, in particular the substantial independence of GDE of conditions in the gas phase. Also DEWHURST, FLAGG AND WATSON[6], by interposing a grid between the electrode and liquid surface, claim to have shown that charged particles are involved in bringing about oxidation.

While there are very close similarities in the chemical effects of GDE and the radiolysis of solutions, particularly when the radiation concerned consists of slow-moving alpha particles, some important differences should also be noted. Although the energies of the bombarding particles in GDE are extremely low *per particle* as compared with any type of ionising radiation, the *dose-rate* is very much greater. Thus with a current of 0.075 A the number of univalent gaseous ions reaching the solution surface per minute is 2.8×10^{19} and, assuming them to have an average energy of 100 eV, this corresponds to a dose-rate of 2.8×10^{21} eV/min. The ionising radiations employed in conventional radiation chemistry have energies in excess of 10^4 eV, but the dose-rates which can be achieved are only of the order 10^{16}–10^{20} eV/ml min. In consequence of the high dose-rate the energy put into the solution in a typical GDE experiment is about 10^{21} eV/ml, while in radiolysis experiments doses of about 10^{18} eV/ml are common. The amount of chemical change in GDE is thus much greater than in radiolysis and the concentrations of substrate which are convenient to use are much higher. Thus in GDE the substrate is able to diffuse into and scavenge the region where the radicals are being formed, and the characteristic feature of the phenomenon is the marked dependence of the nature and quantity of the products on the substrate concentration. In the radiolysis of solutions, the concentrations of solute are usually kept low so that such scavenging within the tracks of the ionising particles is minimised. Secondly, in GDE the dose is confined to a very small reaction zone, whereas in alpha and gamma radiolysis the chemical reactions take place both homogeneously in the bulk of the solution and heterogeneously in the transient hot-spots of activity or spurs (life-time *ca.* 10^{-9} sec). In the steady-state condition which is achieved in GDE, the profile of the free radical concentrations will show a continuous variation from a high value in the surface to zero at a short distance within the solution. Thus all reaction will occur in a heterogeneous region and will arise from the penetration of the substrate up the concentration gradient. This will account for the absence of a "concentration independent" region and will mean that the distinction between radical and molecular yields will lose much of its significance.

SUMMARY

The methods and results of glow-discharge electrolysis have been reviewed and an attempt has been made to pick out the essential features of the process. It is interpreted as a form of electrolysis in which energy transfer as well as charge transfer is involved, and this serves to break up solvent molecules into reactive radicals which produce the chemical reactions observed. The energy is conveyed by gaseous ions accelerated in the electrical field near the liquid surface, and the process has much in common with radiolysis in which the individual particles are of low energy but the dose-rate is extremely high.

ACKNOWLEDGEMENT

Our thanks are due to the Department of Scientific and Industrial Research for a maintenance grant to M.D.I.

REFERENCES

1 J. Gubkin, *Ann. Physik*, [III] 32 (1887) 114.
2 K. Klüpfel, *Ann. Physik*, [IV] 16 (1905) 574.
3 A. Makowetsky, *Z. Elektrochem.*, 17 (1911) 217.
4 A. Klemenc *et al.*, *Z. Elektrochem.*, 20 (1914) 485; 37 (1931) 742. *Z. Physik. Chem.*, 130 (1927) 378; 154 (1931) 385; 166 (1933) 343; 27B (1935) 369; 179 (1937) 1; 182 (1938) 91; 40B (1938) 252; 183 (1938) 217, 297. *Z. Anorg. Allgem. Chem.*, 240 (1939) 167. *Monatsh.*, 75 (1944) 42; 76 (1946) 38; 78 (1948) 243; 81 (1950) 122; 82 (1951) 708, 869, 1041; 84 (1953) 365, 498, 1053; 85 (1954) 47; *Chimia (Aarau)*, 6 (1952) 177. *Z. Elektrochem.*, 56 (1952) 198, 634, 917; 57 (1953) 615.
5 S. Glasstone and A. Hickling, *J. Chem. Soc.*, (1934) 1772. R. A. Davies and A. Hickling, *J. Chem. Soc.*, (1952) 3595. A. Hickling and J. K. Linacre, *J. Chem. Soc.*, (1954) 711. A. R. Denaro and A. Hickling, *J. Electrochem. Soc.*, 105 (1958) 265. A. Hickling and G. R. Newns, *Proc. Chem. Soc.*, (1959) 368; *J. Chem. Soc.*, (1961) 5177, 5186.
6 W. R. Cousins, *Z. Physik. Chem.*, 4B (1929) 440. N. Thon, *Compt. Rend.*, 197 (1933) 1114.

W. Braunbek, *Z. Physik.*, 91 (1934) 184. F. Fichter and K. Kestenholz, *Helv. Chim. Acta*, 23 (1940) 209. A. Muta *et al.*, *J. Electrochem. Soc. Japan*, 17 (1949) 74, 113, 202, 235, 265, 298; 18 (1950) 17, 82. M. Haïssinsky and A. Coche, *J. Chim. Phys.*, 51 (1954) 581. B. S. R. Sastri. *J. Sci. Ind. Res. (India)*, 19B (1960) 317. H. A. Dewhurst, J. F. Flagg and P. K. Watson, *J. Electrochem. Soc.*, 106 (1959) 366. G. H. Cady, H. J. Emeleus and B. Tittle, *J. Chem. Soc.*, (1960) 4138. E. H. Brown, W. D. Wilhide and K. L. Elmore, *J. Org. Chem.*, 27 (1962) 3698.

7 P. de Beco, *Compt. Rend.*, 207 (1938) 623; 208 (1939) 797. *Bull. Soc. Chim. France*, 12 (1945) 779, 789, 795. V. I. Pavlov, *Compt. Rend. Acad. Sci. U.S.S.R.*, 43 (1944) 236, 383, 385.

8 A. Hickling and M. D. Ingram, *Trans. Faraday Soc.*, 60 (1964) 783.

9 A. Klemenc (1946)[4]; R. A. Davies and A. Hickling (1952)[5].

10 United States Patent, 2,632,729 (1953).

11 British Patent, 896,113 (1962).

12 A. Hickling and J. V. Shennan, unpublished work.

13 H. A. Barton and J. H. Bartlett, *Phys. Rev.*, 31 (1928) 823; H. D. Smyth and D. W. Mueller, *ibid.*, 43 (1933) 116; M. M. Mann, A. Hustrulid and J. T. Tate, *ibid.*, 58 (1940) 340.

14 R. M. Chaudrhi and M. L. Oliphant, *Proc. Roy. Soc. (London), Ser. A*, 137 (1932) 662.

15 A. O. Allen, *The Radiation Chemistry of Water and Aqueous Solutions*, Van Nostrand, 1961.

16 G. H. Gore, A. Hickling and M. D. Ingram, unpublished work.

Short Communication

A note on the design and handling of a stationary drop electrode

Several authors[1-4] have published descriptions of the construction of stationary drop electrodes. The principle of this type of electrode is well known and its application in the elucidation of electrode processes and in analytical chemistry has already been described[5-6].

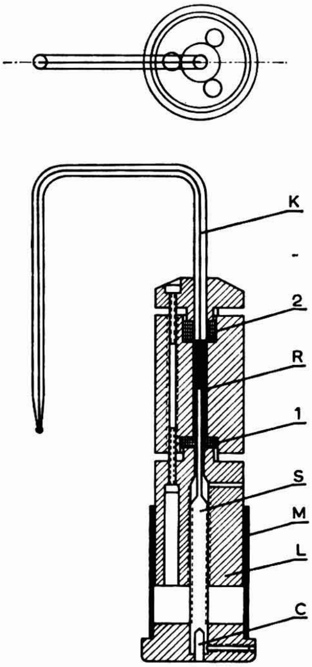


Fig. 1. Stationary drop electrode. K, capillary; R, reservoir; S, screw with the piston; L, nut; M, mantle with scale; C, plug socket; 1 and 2, packings.

An ideal electrode of this type should fulfil the following conditions.

(1) The surface of the mercury drop that forms the electrode should be well reproducible.

(2) The material, from which the electrode is built, and which contacts mercury, should not contaminate the mercury surface by surface-active substances.

(3) The electrode should be insensitive to changes in ambient temperature.

(4) The electrode should be robust and at the same time easily handled.

(5) The capillary should be easily replaceable.

(6) The electrode should permit working with small quantities of amalgams prepared independently of the electrode.

In this note, an electrode fulfilling these conditions, is described. A preliminary description of this type of the electrode has been given in the review by **Říha**[5].

The electrode (Fig. 1) consists of the following main parts: a capillary (K), a reservoir (R), and a nut (L) with screw (S) and piston. The reservoir and nut are made of plexiglass and the piston-with-screw of stainless steel. The packing (1 and 2) is made of teflon. The outer diameter of the reservoir is 30 mm, the inner 3 mm, and the diameter of the piston is usually 2 mm. The pitch of the screw is 0.7 mm. The shift of the piston can be read on the scale engraved on the mantle (M). The nut is connected with the reservoir by means of three screws. Fastening of the screws results in the deformation of the packing which in turn ensures an air-tight passage of the piston. The capillary is fixed in the reservoir in a similar way. The side hole in the nut enables mercury which can accidentally enter this space during filling, to be removed. Electrical contact with mercury is ensured by the piston; the lower end of the screw has the form of a plug socket (C). The inner diameter of the capillary is usually 0.1–0.2 mm, the last 20 mm of length being drawn out to a diameter of about 0.08 mm. For some work it is useful to treat the capillary with silicone, in the usual way for making glass hydrophobic.

When first filling the electrode with mercury or when exchanging the capillary, the piston is shifted towards the lower end of the reservoir. The space above the piston is fully filled with mercury, the capillary is carefully put in, and by fastening the screws in the upper part of the reservoir, the reservoir is closed. This operation usually allows sufficient removal of the air which can easily be checked by observing that during regular turning of the screw a drop is uniformly formed at the orifice of the capillary. If some air has been left in the reservoir, the drop is formed instantaneously, because the space filled with air is first compressed and only after reaching a certain pressure is the drop formed. The presence of air in the reservoir results in decrease of reproducibility. Another criterion of the adequate filling of the electrode is stability (constant position) of the meniscus when the electrode is turned upwards. When the electrode has not been correctly filled, the rest of the air is best removed by turning the screw in such a direction as to draw mercury back into the reservoir. The orifice of the capillary is tightly connected with a well-fitting injection syringe and the space inside the capillary and reservoir is evacuated. By turning the screw in the opposite direction mercury is pressed into the evacuated space. Refilling of mercury into the reservoir is carried out by sucking in mercury from a flask or beaker placed under the tip of the capillary and shifting the piston towards the bottom of the reservoir. When the electrode is not in use, the orifice should first be washed with distilled water by alternate sucking in and out, then the tip of the capillary cleaned with a filter paper, and finally the meniscus drawn some 10 mm above the orifice and the capillary left to dry in the air.

When these principles for handling the electrode are followed, the drop of mercury is firmly held at the orifice of the capillary and the surface of the drop is reproducible to 1%.

For work with small volumes of amalgams (prepared separately) a capillary which is 2 or 3 times longer and without the drawn-out end, is used. A small known volume of amalgam is sucked into the capillary, (but it is not allowed to enter the reservoir).

A part of this amalgam is used for experiments, the rest is pressed out of the capillary by the pressure of pure mercury.

Several years experience with this electrode has shown that it functions satisfactorily for most analytical and theoretical applications.

Polarographic Institute,
Czechoslovak Academy of Science,
Prague (Czechoslovakia)

J. J. VOGEL

1 J. E. B. RANDLES AND W. WHITE, *Z. Elektrochem.*, 59 (1955) 669.
2 W. KEMULA AND Z. KUBLIK, *Anal. Chim. Acta*, 18 (1953) 104.
3 J. J. VOGEL, *Czechoslovak–Hungarian Polarographic Conference, Praha, July 1958.* Abstr., Polarog. Inst., Czech. Acad. Sci., Praha.
4 F. v. STURM AND M. RESSEL, *Z. Anal. Chem.*, 186 (1962) 63.
5 J. ŘÍHA, *The Hanging Mercury Drop in Polarography*, in *Progress in Polarography*, edited by P. ZUMAN AND I. M. KOLTHOFF, Interscience Publishers Inc., 1962.
6 W. KEMULA AND Z. KUBLIK, *Application of Hanging Mercury Drop Electrodes in Analytical Chemistry*, in *Advances in Analytical Chemistry and Instrumentation*, Vol. 2, edited by C. N. REILLEY, Interscience Publishers Inc., New York, 1963.

Received April 6th, 1964

Book Review

The Modern Theory of Molecular Structure, by B. PULLMAN, Dover Publications Inc., New York, 1962, vii + 87 pages, $1.00.

This is a very short monograph which deals with modern theories of molecular structure developed since Planck's discovery of the quantization of energy. It is primarily designed for those chemists who have not sufficient time to study the rather complicated mathematical treatment which is necessary for a deeper insight into the structure and reactivity of chemical compounds. Prof. B. PULLMAN can be considered one of the most able teachers in this field and also one of the most active investigators. He has the rare talent of putting the rather difficult concepts and theories into a more easily understandable form so that this short book can be warmly recommended to all those who wish to have an idea of modern theoretical chemistry, but do not have time to make a detailed study of it.

G. MILAZZO, Istituto Superiore di Sanità, Rome

Correction

In the article THE USE OF PROGRAMMED CURRENT CHRONOPOTENTIOMETRY IN STUDIES OF ADSORPTION, *J. Electroanal. Chem.*, 7 (1964) 242, equation (3) should read:

$$\tau^{\frac{3}{2}} - \frac{3\pi^{\frac{1}{2}}\tau K}{4D^{\frac{1}{2}}} + \cdot\cdot\cdot\cdot\cdot$$

ROYCE W. MURRAY

CONTENTS

Original papers

The contribution of electrostatic coupling to electrical migration in chronopotentiometry
M. D. MORRIS (Cambridge, Mass., U.S.A.) 1

The influence of hydrolysis on the deposition and co-deposition of iron-group metals (Fe, Co, Ni) at the dropping mercury electrode
H. DAHMS (Yorktown Heights, N.Y., U.S.A.) 5

Mesure directe des coefficients de diffusion d'ions en solution aqueuse en présence d'un électrolyte support
A. M. BATICLE (Bellevue (S. et O.), France) 13

Effects of anions and cations on oxygen reduction and oxygen evolution reactions on platinum electrodes
A. KOZAWA (Cleveland, Ohio, U.S.A.). 20

Derivative polarographic titration of tertiary amines and salts of organic acids in acetic acid in the presence of antimony and quinhydrone electrodes
V. VAJGAND AND T. PASTOR (Belgrade, Yugoslavia) 40

Determination of tertiary amines and salts of organic acids in glacial acetic acid by dead-stop method
V. VAJGAND AND T. PASTOR (Belgrade, Yugoslavia) 49

Electrochemical behavior of copper ions and silver ion in hydracrylonitrile and some related nitriles
F. FARHA, JR. AND R. T. IWAMOTO (Lawrence, Kan., U.S.A.) 55

Review

Glow-discharge electrolysis
A. HICKLING AND M. D. INGRAM (Liverpool, England) 65

Short communication

A note on the design and handling of a stationary drop electrode
J. J. VOGEL (Prague, Czechoslovakia). 82

Book review 84

Correction 84

ELSEVIER PUBLISHING COMPANY, AMSTERDAM
Printed in The Netherlands by
NEDERLANDSE BOEKDRUK INRICHTING N.V., 'S-HERTOGENBOSCH

ELSEVIER PUBLICATIONS ON CHEMISTRY

MODERN METHODS OF ANALYSIS OF COPPER AND ITS ALLOYS — Second revised edition

by Charles M. DOZINEL, Consulting Chemist, Brussels
Translated by Stephanie L. Man, London

CONTENTS: 1. Spectrographic method. 2. Chemical wet methods (General). 3–26. Determination of copper, lead, tin, iron, nickel, manganese, aluminium, zinc, cadmium, phosphorus, silicon, arsenic, antimony, bismuth, selenium/tellurium, chromium, silver, beryllium, carbon, cobalt, sulphur, titanium, magnesium, special elements. 27. Inclusions, gases. 28. Combined procedures. 29. Miscellaneous.

× 9″ xviii + 288 pages 36 tables 15 illustrations 1116 references 1963 £ 4.0.0.

COLORIMETRIC DETERMINATION OF ELEMENTS — Principles and Methods

by G. CHARLOT, Professor of Analytical Chemistry, Faculté des Sciences, Ecole Supérieure de Physique et de Chimie Industrielles, Paris

CONTENTS: PART I: THEORETICAL BACKGROUND (13 chapters). PART II: ESTIMATION OF THE PRINCIPAL ELEMENTS:
Aluminium. Antimony. Arsenic. Barium. Beryllium. Bismuth. Boron. Bromine. Bromides. Cadmium. Calcium. Carbon and its compounds. Cerium. Cesium. Chlorine and its compounds. Chromium. Cobalt. Copper. Fluorine. Gallium. Germanium. Gold. Hydrogen. Indium. Iodine. Iridium. Iron. Lead. Lithium. Magnesium. Manganese. Mercury. Molybdenum. Nickel. Niobium, Tantalum. Nitrogen and its compounds. Osmium. Oxygen and its compounds. Palladium. Phosphorus. Platinum. Potassium. Rare earth metals. Rhenium. Rhodium. Rubidium, cesium. Ruthenium. Scandium. Selenium, tellurium. Silicon. Silver. Sodium. Strontium. Sulphur and its compounds. Tantalum. Technetium. Tellurium. Thallium. Thorium. Tin. Titanium. Tungsten. Uranium. Vanadium. Zinc. Zirconium. Index.

6½ × 9½″ xii + 450 pages 12 tables 72 illustrations 1964 £ 5.0.0.

PHYSICO-CHEMICAL CONSTANTS OF PURE ORGANIC COMPOUNDS, VOLUME 2

by J. TIMMERMANS, Director of the International Bureau of Physico-Chemical Standards; Professor of Physical Chemistry, Université Libre, Brussels

CONTENTS: 1. Hydrocarbons. 2. Halogenated derivatives. 3. Oxygenated derivatives of the aliphatic series. 4. Oxygenated derivatives of the aromatic series. 5. Oxygenated derivatives of polymethylenes. 6. Heterocyclic oxygen compounds. 7. Sugars. 8. Mixed oxyhalogenated derivatives. 9. Nitrogen derivatives of the aliphatic series. 10. Nitrogen derivatives of the cyclic series. 11. Oxygen and nitrogen derivatives. 12. Mixed halogen–nitrogen derivatives. 13. Sulphur derivatives. 14. Derivatives with other elements. Index.

6½ × 9½″ approx. 450 pages 430 literature references 1964 £ 6.0.0.

ELSEVIER PUBLISHING COMPANY
AMSTERDAM LONDON NEW YORK

278E

93223