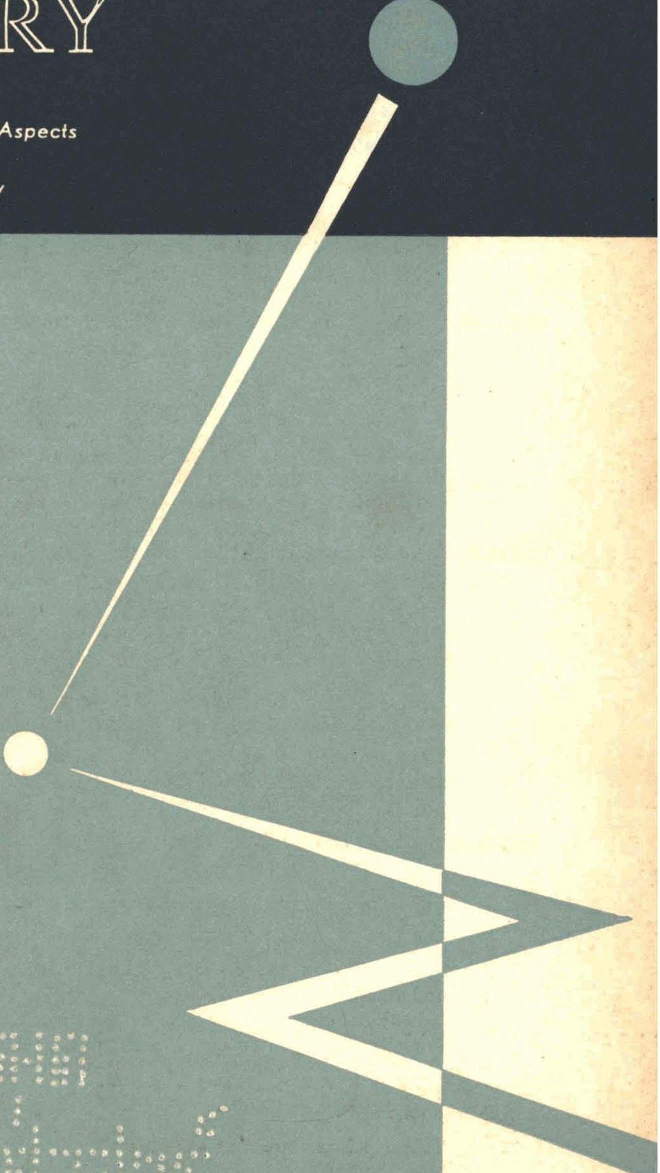
VOL. 8 NO. 6 DECEMBER 1964
PUBLISHED MONTHLY

Journal of

# ELECTROANALYTICAL CHEMISTRY

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



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# IMMUNO-ELECTROPHORETIC ANALYSIS

edited by **P. GRABAR**

Directeur de l'Institut de Recherches Scientifiques sur le Cancer, Villejuif (Seine), France

and **P. BURTIN**

Chef du Laboratoire d'Immunologie à l'Institut de Recherches Scientifiques sur le Cancer, Villejuif (Seine), France

## Applications to Human Biological Fluids

Immuno-electrophoretic analysis, first described in 1953 by Grabar and Williams as a method for the study of antigenic substances, is currently finding application in a wide variety of research and clinical problems. The process combines the principles of zone electrophoresis with those of immunochemical analysis, thus allowing the simultaneous definition of electrophoretic mobility and immunochemical specificity of biological fluid. In addition, staining and enzymatic reactions may be carried out in the same gelified medium, thereby adding a third dimension to the analysis. This method is at present enjoying general use and this volume comprises almost all the data currently available which is relevant to the study of human material.

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PART II APPLICATIONS TO HUMAN PLASMA

5. The proteins of normal human plasma. 6. Immuno-electrophoretic analyses of umbilical cord blood and of the blood of infants. 7. Immuno-electrophoretic control of the fractionation of plasma. 8. Introduction to the study of pathological sera. 9. The agammaglobulinemias. 10. The immuno-electrophoretic study of myeloma proteins. 11. Immuno-electrophoretic analysis of the macroglobulins in Waldenström's disease. 12. The cryoglobulinemias. 13. The hepatic diseases. 14. Immuno-electrophoretic studies of serum from rheumatics. 15. Immuno-electrophoretic analysis of the serum in leukemias and sarcomas. 16. Immuno-electrophoretic study of the serum during the course of systemic lupus erythematosus. 17 Various diseases. 18. Conclusions from studies of pathological sera by immuno-electrophoresis.

PART III STUDIES ON OTHER HUMAN MEDIA

19. Studies on other human media. 20. Immuno-electrophoretic study of proteinurias. 21. The proteins of the cerebro-spinal fluid. 22. Perilymphatic liquid. 23. The nature of the synovial fluid proteins. 24. Immuno-electrophoretic studies of the proteins of human milk and colostrum. 25. Immuno-electrophoretic studies of human amniotic fluid, meconium and infant stool. 26. The seminal fluid. 27. Applications of immuno-electrophoretic analysis to the study of the formed elements of the blood.

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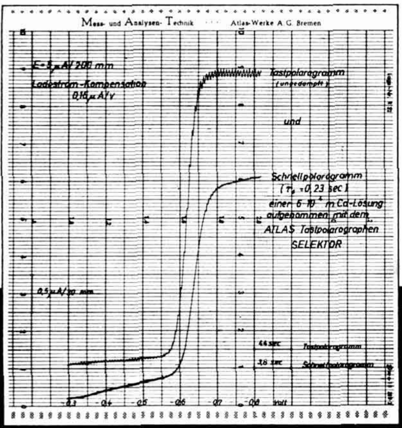

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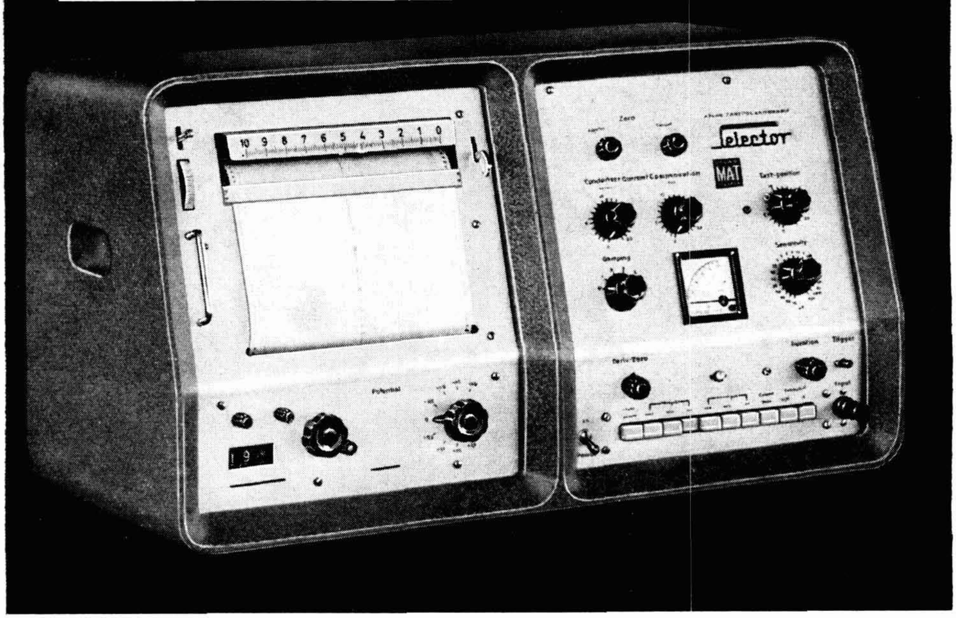

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# SUMMARIES OF PAPERS PUBLISHED IN JOURNAL OF ELECTROANALYTICAL CHEMISTRY

Vol. 8, No. 6, December 1964

## THE DEPENDENCE OF THE STANDARD POTENTIALS OF GALVANIC CELLS ON THE DIELECTRIC CONSTANTS OF SOLVENTS

An expression is developed using the concepts of electrostatics to account for the dependence of the standard potentials of cells on the dielectric constants of solvents. The expression is tested using data on cells involving bi-univalent electrolytes and found to give satisfactory results. Cells involving an uni-univalent electrolyte, hydrochloric acid gave standard electrode potential–reciprocal of the dielectric constant plots which showed curvature in the lower dielectric regions of the solvent, but which approached linearity in the higher dielectric constant regions. The data in this higher dielectric constant region conformed well with theory.

E. S. Amis,

*J. Electroanal. Chem.*, 8 (1964) 413–418.

## A STUDY OF TRANSFERENCE AND SOLVATION PHENOMENA OF LITHIUM CHLORIDE IN WATER AND WATER–DIOXANE SOLVENTS

Transference and solvation phenomena for the ions of lithium chloride in water and water–dioxane solvents have been studied. The transference numbers of the anion as a function of salt concentration in water and as a function of solvent composition are presented graphically and discussed in relation to relative solvation of the lithium and chloride ions. The amount of solvent transferred from the anode to the cathode is presented graphically and discussed.

J. R. Bard, J. O. Wear, R. G. Griffin and E. S. Amis,

*J. Electroanal. Chem.*, 8 (1964) 419–424.

## A PRELIMINARY INVESTIGATION ON DERIVATIVE CYCLIC CONSTANT CURRENT VOLTAMMETRY

A new electroanalytical method, Derivative Cyclic Constant Current Voltammetry (DCCCV), has been described. Its application to qualitative and quantitative analysis as well as to investigations of differential double layer capacitance has been discussed.

A multipurpose instrument utilizing operational amplifiers has been described. The instrument can be used for conventional, current reversal, and cyclic chronopotentiometry as well as for the new method. In addition, the instrument can serve as a generator of square, triangular, and saw-tooth waves.

P. E. Sturrock,

*J. Electroanal. Chem.*, 8 (1964) 425–433.

## NICKEL(IV) DIMETHYLGLYOXIME

The red solutions of nickel dimethylglyoxime in strongly basic solution have been studied by electrochemical, spectrophotometric and magnetic methods. It is concluded that the red complex is a species of Ni(IV). A controlled potential coulometric method for the analysis of nickel is also presented.

D. G. Davis and E. A. Boudreaux,
*J. Electroanal. Chem.*, 8 (1964) 434–441.

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## DROP-TIME DEPENDENCE OF A.C. POLAROGRAPHIC PEAK HEIGHTS

Experimental evidence of the drop-time dependence of the peak height in a.c. polarography is presented for a quasi-reversible electron-transfer process and a number of reductions and oxidations involving coupled chemical reactions, rate limited surface coverage, and amalgam formation. Each process is discussed in relation to the kinetics of the overall electrode reaction. In the systems reported, drop-time dependence is exhibited whenever a form of mass transfer other than, or as well as, diffusion operates.

G. H. Aylward and J. W. Hayes,
*J. Electroanal. Chem.*, 8 (1964) 442–448.

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## ISOTHERMS FOR HYDROGEN ADSORPTION ON PLATINUM ELECTRODES IN SULFURIC ACID SOLUTION

The applicability of a Langmuir type isotherm and of a Frumkin type isotherm to each of the different regions of hydrogen adsorption on smooth platinum in 1 $N$ $H_2SO_4$ was tested between 0° and 70° by comparing experimental and computed current–potential curves at anodic potentials in the region of hydrogen adsorption. The values of the parameters used in the computation were taken from the experimental data. While the Langmuir isotherm yields acceptable results only for $T < 20°$, the Frumkin isotherm allows an approximation in the studied temperature range. The decrease of the free energy of adsorption with coverage for the strongly bonded hydrogen in the studied temperature range and for the weakly bonded hydrogen at $T > 50°$ is interpreted as a tendency to hydride formation.

M. W. Breiter,
*J. Electroanal. Chem.*, 8 (1964) 449–453.

## THE POLAROGRAPHY OF *trans*-DINITROBIS(ETHYLENEDIAMINE)COBALT(III) ION IN BUFFERED SOLUTIONS

### THE MECHANISM OF THE FORMATION OF THE DOUBLE WAVE

The effect of pH and $NO_2^-$ concentration on the polarography of *trans*-$[Co(en)_2(NO_2)_2]^+$ has been studied. The polarographic waves have been interpreted on the basis of the following mechanisms.

Wave I.

$$[Co(en)_2(NO_2)_2]^+ + 1\ e \rightleftharpoons [Co(en)_2(NO_2)_2]$$

$$[Co(en)_2(NO_2)_2] \rightleftharpoons [Co(en)_2(NO_2)]^+ + NO_2^-$$

$$[Co(en)_2NO_2]^+ \rightleftharpoons Co(en)_2^{2+} + NO_2^-$$

$$Co(en)_2^{2+} \xrightarrow{\text{decomposition}}$$

Wave II.

$$2\ Co(en)_2^{2+} \rightleftharpoons Co(en)_3^{3+} + Co(en)^{2+} + 1\ e$$

J. G. Mason and R. L. White,
*J. Electroanal. Chem.*, 8 (1964) 454–462.

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## THE POLAROGRAPHIC REDUCTION OF METAL COMPLEXES

When a metal present as the complex $MX_q$ is polarographically reduced in the absence of excess complexing agent the equation of the wave at 25° is given by

$$E_{\text{dme}} = E' - \frac{0.0591q}{n} \log \frac{K_a}{C_h + K_a} - \frac{0.0591}{n} \log \frac{i^{q+1}}{i_d - i}$$

The wave is consequently unsymmetrical about its midpoint and the reduction potential will be pH-dependent over a range of pH depending on the value of $K_a$ (the acid dissociation constant of the complexing agent).

A comparison of the above case with that which applies when complexing agent is present in excess yields a relationship which may lead to the evaluation of the polarographic diffusion coefficient of the complexing ion.

Some supporting experimental evidence is presented.

C. G. Butler and R. C. Kaye,
*J. Electroanal. Chem.*, 8 (1964) 463–471.

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## PHASE ANGLE TITRATION: A NEW ELECTROANALYTICAL TECHNIQUE

*(Short Communication)*

U. H. Narayanan, G. Dorairaj and Y. Mahadeva Iyer,
*J. Electroanal. Chem.*, 8 (1964) 472–475.

## EFFECT OF JUNCTION POTENTIALS AT THE SALT BRIDGE ON THE MEASURED VALUES FOR THE HALF-WAVE POTENTIAL OF THE $Pb^{2+} \rightarrow Pb^0$ REDUCTION IN AQUEOUS SOLUTIONS OF HYDROCHLORIC ACID AND POTASSIUM CHLORIDE

*(Short Communication)*

W. L. Belew and H. P. Raaen,

*J. Electroanal. Chem.*, 8 (1964) 475–477.

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## AMPEROMETRIC TITRATION OF ZINC WITH POTASSIUM FERROCYANIDE BY A.C. POLAROGRAPHY

*(Short Communication)*

S. L. Gupta and S. K. Sharma,

*J. Electroanal. Chem.*, 8 (1964) 478–480.

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## POLAROGRAPHIC DETERMINATION OF SILVER IN GOLD

*(Short Communication)*

J. R. Luck and E. H. Lindemann,

*J. Electroanal. Chem.*, 8 (1964) 480–482.

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## THE ELECTRODE POTENTIAL OF SILVER AND SILVER–SILVER HALIDE ELECTRODES

*(Short Communication)*

E. M. Khairy, Mrs. Afaf El-Said Mahgoub,

*J. Electroanal. Chem.*, 8 (1964) 482–485.

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## THE SIGNIFICANCE OF MEASUREMENTS BY THE TRIANGULAR SWEEP METHOD APPLIED TO ADSORPTION REACTIONS

*(Short Communication)*

The kinetics of charging processes producing or removing adsorbed intermediates are examined for the case of linearly varying, potentiostatically controlled electrode potential (voltage sweep method). The adsorption capacitance as a function of potential and sweep rate is deduced and related to the *equilibrium* capacitance. Only a complex relation results. The galvanostatic method, however, leads to a much simpler relation between capacitance, equilibrium capacitance and charging rate. It is concluded that the sweep method cannot give quantitatively useful kinetic information in complex reactions where Faradaic and pseudo-Faradaic currents are involved as a function of potential.

B. E. Conway,

*J. Electroanal. Chem.*, 8 (1964) 486–489.

# THE DEPENDENCE OF THE STANDARD POTENTIALS OF GALVANIC CELLS ON THE DIELECTRIC CONSTANTS OF SOLVENTS

EDWARD S. AMIS

*Department of Chemistry, University of Arkansas, Fayetteville, Ark. (U.S.A.)*

(Received July 13th, 1964)

CORSARO AND STEPHENS[1] studied the cell

$$\text{Zn–Hg; ZnCl}_2(m),\ (X)(Y);\ \text{AgCl(S); Ag} \qquad (1)$$

in water–methanol, water–ethanol and water–dioxane solvents. They found that the standard potential of the cell in all three solvent systems varied linearly with the reciprocal of the dielectric constant with a precision better than 0.1 mV. All plots extrapolated through the single value, that of the standard cell potential with water. In the cell depicted in eqn. (1), $(X)$ represents the percentage by weight of methyl alcohol, ethyl alcohol, or 1,4 dioxane in water of wt. % $(Y)$.

These authors attribute the linear relationship between $E^0$ and $1/D$ to obedience of the Debye–Hückel theory of the electrolyte in the cell. To obtain this obedience the extended Debye–Hückel theory involving the first power of the ionic strength and, therefore, a semiempirical constant $C'$ had to be used. Since the semiempirical constant $C'$, which takes into account the variation of the dielectric constant of the medium with changing ionic strength, cannot be determined readily from theory, a quantitative test of the obedience of data to theory would be difficult.

HEFLEY AND AMIS[2] investigated the cell

$$\text{Cd–Hg; CdCl}_2(m),\ (X),\ (Y);\ \text{AgCl(S); Ag} \qquad (2)$$

using water, water–methanol, methanol, water–ethanol and ethanol solvents. Standard electrode potentials were linear with respect to the reciprocals of the dielectric constants over the whole range of compositions of solvents at 25°, 30° and 35°C with a precision 0.6 mV.

Representative data is given for water–methanol solvent at 35°C in curve (A) of Fig. 1.

Another cell that has been studied over a range of compositions of solvents is

$$\text{Pt, H}_2;\ \text{HCl}(m),\ (X),\ (Y);\ \text{AgCl; Ag} \qquad (3)$$

where $(X)$ is the wt. % dioxane or methanol in (Y) wt. % water. HARNED AND THOMAS[3] studied the cell when methanol was the nonaqueous component of the solvent and HARNED, WALKER AND CALMON[4] when dioxane was the nonaqueous component. The plots of standard cell potentials *vs.* the reciprocals of the dielectric constants showed curvatures which were most pronounced in the lower dielectric regions but approached lineararity in the higher dielectric regions of the solvents studied. (See curve (B), Fig. (1) for dioxane–water solvents.) The shapes of these curves are reminescent of curves obtained from kinetic data when logarithms of specific velocity constants are plotted against the reciprocals of dielectric constants[5] for certain reactions.

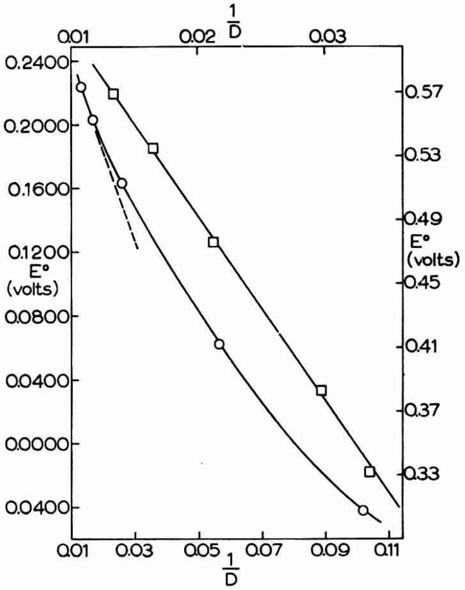

Fig. 1. $E°$ *vs.* $1/D$ for selected cells: □, the cell depicted in eqn. (2) at 35° (upper abscissa and ordinate at the right); ○, the cell depicted in eqn. (3) at 25° (lower abscissa and ordinate at the left).

Harned and Owen[6] for solutions containing $n_i - - - n_j - - - n_s$ ions per cc, added the electrical work ($W'(n)$) for discharging the ions at high dilution in a solvent (water) of dielectric constant $D_0$, and recharging them in a solvent of dielectric $D$, to the electrical work ($W(\varkappa)$) done against the potential due to the ionic atmosphere, and obtained the total electrical work ($W_t$) of the charging process. This total work was set equal to the increase in work content $\Delta A$ of the system giving the equation,

$$\Delta A = W_t = \frac{1}{2D}\sum_{1}^{s}\frac{n_j e_j^2}{b_j} - \frac{1}{2D_0}\sum_{1}^{s}\frac{n_j e_j^2}{b_j} - \frac{\varkappa}{3D}\sum_{1}^{s} n_j e_j^2 \tag{4}$$

In this equation $b_j$ is the radius of the $j$th type of ion considered as a perfect sphere, $e_j$ is the charge on the ion, and $\varkappa$ is the Debye kappa.

Equation (4) can be used to obtain an expression for the effect of a non-electrolyte upon the activity coefficient of an electrolyte at extreme dilution. When the charges from $n$ molecules of electrolyte are transferred from water with dielectric constant $D_0$, to a water–non-electrolyte mixture of dielectric constant $D$, the electrical work

$W_t$ required is

$$\Delta A = W_t = \frac{n'\varepsilon^2}{2D}\sum_1^s \frac{\gamma_j z_j^2}{b_j} - \frac{n'\varepsilon^2}{2D_0}\sum_1^s \frac{\gamma_j z_j}{b_j} \tag{5}$$

where $\gamma_j$ is the number of ions of valence $z_j$ and $\varepsilon$ is the electronic charge. When this electrical work is set equal to the increase in work content and the equation differentiated with respect to $n'$, there results the equation

$$\gamma kT \ln f_{\pm(t)} = \frac{\varepsilon^2}{2D}\sum_1^s \frac{\gamma_j z_j^2}{b_j} - \frac{\varepsilon^2}{2D_0}\sum_1^s \frac{\gamma_j z_j^2}{b_j} \tag{6}$$

or

$$\ln f_{\pm(t)} = \frac{(D_0 - D)\varepsilon^2}{2\gamma kTDD_0}\sum_1^s \frac{\gamma_j z_j^2}{b_j} \tag{7}$$

The term $\ln f_{\pm(t)}$ is the activity coefficient of the electrolyte arising from the primary medium effect. Equation (7) is the equation derived by BORN[7].

The thermal energy term $kT$ is introduced into eqn. (7) by setting the partial differential of the work content with respect to $n'$, $(\partial\Delta A/\partial n')_{P,T,n,D}$ equal to $\gamma kT \ln f_{\pm(t)}$ in eqn. (6).

HARNED AND OWEN replace $\ln f_{\pm(t)}$ in eqn. (7) by the corresponding expression for the electromotive force and obtain for a 1 : 1 electrolyte at 25° the equation

$$\frac{E_N{}^\circ - E_N{}^{\circ *}}{0.05915} = 1.210 \cdot 10^2 \frac{D_0 - D}{DD_0}\sum \frac{1}{b_j} \tag{8}$$

The subscript $N$ indicates that mole fraction is the concentration scale employed. It must be remembered that eqn. (8) resulted by extrapolation to infinite dilution and to a standard reference state of dielectric constant, in this case water. HARNED AND OWEN found the $E_m{}^{\circ *}$ ($m$ indicates the concentration is expressed in molality) *vs.* $1/D$ gave the results discussed in connection with the cell (3). Their plots for higher dielectric constant regions was for $b_j$ values corresponding roughly to those derived from crystallographic radii and for $b_j$ values resulting from a mean ionic diameter of 5 Å (radius of 2.5 Å), if the radii of both ions are assumed to be equal. They conclude that, although the agreement with this rough procedure is not good, nevertheless, the theoretical results are of the right order of magnitude. They believe the phenomenon too complicated to be completely explained by so simple an electrostatic theory. The great deviation from theory at low dielectric constants, they attribute to replacement of the hydronium ion $H_3O^+$ by (solvent) $H^+$ according to the reaction $H_3O^+ + \text{(solvent)} \rightleftharpoons H_2O + \text{(solvent)}\,H^+$.

Let us consider a different approach to this problem which does not involve the thermal energy $kT$. There will still be a temperature dependence of $E^\circ$ due to the fact that the standard reference value of $E^\circ$ selected and the dielectric constant of the medium will both depend on the temperature at which data are taken. The concentration influence will not enter the expressions explicitly, and therefore there will be no reason to specify infinitely dilute solutions. The standard reference state of dielectric constant, as will be shown, can conveniently be taken as $D = \infty$ since at this dielectric constant all charge effects will vanish. The change in Helmholtz and

Gibbs free energies will be the same in these systems where pressure and volume are invarient.

If the influence of the dielectric constant of the medium on the standard potential of a cell can be considered as arising from the difference in work at different dielectric constants necessary to bring the ionic reactants to within a critical distance $r$ of each other, a theoretical equation which can be tested quantitatively may be derived for the dependence of the standard cell potential $E^\circ$ on the reciprocal of the dielectric constant $D$.

The work necessary to bring an ion of charge $z_A$ from infinity to within a distance $r$ of an ion of charge $z_B$ in a medium of dielectric constant $D$ is given by the expression

$$w = -\frac{z_A z_B \varepsilon^2}{KDr} \tag{9}$$

and the work per mole of ions becomes

$$w = -\frac{N z_A z_B \varepsilon^2}{KDr} \tag{10}$$

where $K = 10^7$ ergs per joule.

Let us consider the cell represented in eqn. (2), the electrode and cell reactions of which can be written as

$$\begin{array}{ll} \mathrm{Cd} \rightarrow \mathrm{Cd}^{2+} + 2e & \text{oxidation reaction at the anode} \\ 2\mathrm{Ag}^+ + 2e \rightarrow 2\mathrm{Ag} & \text{reduction reaction at the cathode} \\ \hline \mathrm{Cd} + 2\mathrm{Ag}^+ \rightarrow \mathrm{Cd}^{2+} + 2\mathrm{Ag} & \text{or} \quad \mathrm{Cd(Hg)} + 2\mathrm{AgCl(s)} \rightarrow \mathrm{CdCl_2(m)} + 2\mathrm{Ag(s)} \end{array}$$

The effect of the dielectric constant on the cell reaction can be given in terms of the electrostatic work necessary to bring the reactants to within reaction distance $r$. The total maximum work or free energy change necessary for the process at unit activities of reactants and products is $n\mathscr{F}E^\circ$ where $n$ is the number of electrons involved in the electrode process, *e.g.*, $n = 2$ in the reactions given above, $\mathscr{F}$ is the faraday (96,500 coulombs) and $E^\circ$ is the standard cell potential in volts, *i.e.* the potential when the reactants and products are at unit activity. This work can be considered to be composed of two parts; a part arising from the reaction freed from charge effects, which we will call $E_1^\circ$, and a part representing the electrostatic contribution to the work, $E_2^\circ$. Hence the maximum work or free energy change for the cell process per mole is

$$n\mathscr{F}E^\circ = n\mathscr{F}E_1^\circ + n\mathscr{F}E_2^\circ \tag{11}$$

but

$$n\mathscr{F}E_2^\circ = -\frac{N z_A z_B \varepsilon^2}{DrK} \tag{12}$$

therefore

$$n\mathscr{F}E^\circ = n\mathscr{F}E_1^\circ - \frac{N z_A z_B \varepsilon^2}{DrK} \tag{13}$$

and

$$E^\circ = E_1^\circ - \frac{N z_A z_B \varepsilon^2}{n\mathscr{F}DrK} \tag{14}$$

This derivation is general for all cells. From eqn. (14) if $E^\circ$ is plotted against $1/D$ a straight line should result with a slope equal to $(-Nz_Az_B\varepsilon^2/n\mathcal{F}rK)$ and an intercept equal to $E_1^\circ$.

From the slope of this line a value of $r$ which should approach molecular dimensions should be obtained. The reasonableness of this value of $r$ constitutes a quantitative test of the theory. In Table I are listed values of $r$ calculated in this manner. The values are gratifying, if somewhat small, and support the authenticity of the theoretical approach. It is noticeable that reasonable values of $r$ are obtained for different electrolytes, at different temperatures in different solvents. There is evidence of some specific solvent effect for different solvents even with the same electrolyte. This is similar to the observations in the case of kinetic phenomena[5]. It should be mentioned that in the cases of the cells involving hydrochloric acid, the slopes of the $E^\circ$ *vs.* $1/D$ curves were taken at the higher dielectric constant, more nearly straight portions of the curves as indicated for curve (B), Fig. 1. This is the procedure used in the case of kinetic phenomena[5].

TABLE 1

VALUES OF $r$ CALCULATED FROM THE SLOPES OF $E^\circ$ *vs.* $1/D$ PLOTS FOR CELLS COMPOSED OF DIFFERENT ELECTROLYTES AND DIFFERENT ELECTRODE SYSTEM

| *Salt* | *Solvent system* | *Temp. (°C)* | $r$ (Å) |
|---|---|---|---|
| $CdCl_2$ | $H_2O$–MeOH | 25 | 1.18 |
| | | 30 | 1.20 |
| | | 35 | 1.22 |
| $CdCl_2$ | $H_2O$–EtOH | 25 | 1.32 |
| | | 30 | 1.36 |
| | | 35 | 1.34 |
| $ZnCl_2$ | $H_2O$–dioxane | 25 | 2.08 |
| | $H_2O$–MeOH | 25 | 0.94 |
| | $H_2O$–EtOH | 25 | 1.06 |
| HCl | $H_2O$–dioxane | 25 | 2.77 |
| | $H_2O$–MeOH | 25 | 0.64 |

The values of $E_1^\circ$ could be obtained from calculations using eqn. (14) or from extrapolation of the $E^\circ$ *vs.* $1/D$ plots to $1/D = 0$, or $D = \infty$. For example, the $E_1^\circ$ at 25° for the cell depicted in curve (A) of Fig. 1 is found from extrapolation to be 0.3740 V. This relatively high voltage indicates that the cell potentials of galvanic cells freed from electrostatic effects among the ions of the electrolyte of the cell would be considerably greater than the potential observed in the actual case where electrostatic effects do occur. Much work is involved in separating the ions due to their charges and this work does not appear as available work in the actual case.

The upward curvature of the $E^\circ$ *vs.* $1/D$ curve at lower dielectric constants in the case of cells containing hydrochloric acid is probably due to the selective solvation of, or selective solvent binding, by the ions of the higher dielectric, more polar, component of the solvent, in this case water. This probably is especially true in solutes furnishing the hydrogen ion due to strong hydrogen bonding and the formation of $H_3O^+$ and $H_9O_4^+$ ions with water[8].

The anion, however, is probably also selectively solvated by the more polar component of the solvent. This selective solvation (or solvent binding) continues to be influential until only a small amount of water remains in the solvent[9]. The behavior of the ions in the mixed solvents tends toward their behavior in the pure component with which they are most closely associated in the mixed solvents. This effect has been observed in rate phenomena[10]. The water having the higher dielectric constant, is the more polar component of the solvent, and being more intimately associated with the ions, permits their more ready dissociation, or reduces their attraction for each other. Therefore, less work than expected at the lower dielectric constants is required to free the ions of opposite charge from each other's influence. Hence more work than expected becomes available for external use. This increase of available work is manifested as a higher potential than would be expected from the electrostatic forces between the ions of opposite charge at the lower dielectric constants.

## ACKNOWLEDGEMENT

The author wishes to thank the United States Atomic Energy Commission whose financial support of Contract AT-(40-1)-2069 made this work possible.

## SUMMARY

An expression is developed using the concepts of electrostatics to account for the dependence of the standard potentials of cells on the dielectric constants of solvents. The expression is tested using data in cells involving bi-univalent electrolytes and found to give satisfactory results. Cells involving an uni-univalent electrolyte, hydrochloric acid gave standard electrode potential–reciprocal of the dielectric constant plots which showed curvature in the lower dielectric regions of the solvent, but which approached linearity in the higher dielectric constant regions. The data in this higher dielectric constant region conformed well with theory.

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# A STUDY OF TRANSFERENCE AND SOLVATION PHENOMENA OF LITHIUM CHLORIDE IN WATER AND WATER–DIOXANE SOLVENTS*

JAMES R. BARD
*Shell Oil Company, Houston, Texas (U.S.A.)*

JAMES O. WEAR
*Sandia Laboratory, Albuquerque, N. M. (U.S.A.)*

ROBERT G. GRIFFIN AND EDWARD S. AMIS
*University of Arkansas, Fayetteville, Ark. (U.S.A.)*

(Received August 22nd, 1964)

In all previous investigations in this series[1-5] of transport and solvation phenomena, the solvents have been mixtures of water and ethanol. In this work water–dioxane mixtures have been used as it was thought that the use of an organic solvent component that did not resemble water would provide more information about the process of solvation. Lithium chloride was the solute chosen for this study since it had previously been used in water–ethanol mixtures[3] and is reasonably soluble in dioxane–water mixtures. The system could be studied only to 84% by weight of dioxane because a water–dioxane–LiCl system separates into two layers in this region[6]. A Hittorf transference measurement wih the use of an inert reference substance was the method chosen for the determination of the transport and solvation data. This same method was used in our previous studies[1-6].

## EXPERIMENTAL

The lithium chloride was J. F. Baker Analytical Reagent. The dioxane was Fisher Certified Reagent. The inert reference substance, α-methyl-D-glucoside, was prepared by Matheson, Coleman and Bell and was of the highest purity. The silver wire and all other chemicals were of reagent quality. The experimental procedure used has already been described[1,2].

## TREATMENT OF DATA

The symbols used in this paper are the same** as were used in the study of lithium chloride in water–ethanol solvents[3].

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* This work was supported by the United States Atomic Energy Commission. Reproduction in whole or in part is permitted for any purpose of the U. S. Government. The experimental work was performed at the University of Arkansas, Fayetteville, Arkansas (U.S.A.)
** See APPENDIX

The Hittorf transference numbers of the cation and anion, and the grams of solvent transferred per faraday of electricity from the anode to the cathode were calculated using the following equations:

$$t_c' = \left(\frac{p_s^m}{100 - p_s^m} - \frac{p_s^a}{100 - p_s^a}\right) \frac{W(100 - p_s^a)\, A_{\mathrm{Ag}}}{100\, W_{\mathrm{Ag}}} \tag{1}$$

$$t_c = t_c' + \frac{\lambda_c}{\lambda_c + \lambda_a} t_{\mathrm{OH}^-} \tag{2}$$

$$\Delta G^F_{\mathrm{sol}} = \frac{\left(\alpha_a \dfrac{d_m}{d_a} - \alpha_m \dfrac{1 - f_s^a}{1 - f_s^m}\right) W}{F \alpha_m} \tag{3}$$

where $t_c'$ is the measured cation transference number, and $t_c$ the cation transference number corrected for the presence of hydroxyl ion, which is present because a silver cathode was used in place of a silver–silver chloride cathode. This correction is only important at low concentrations since the hydroxyl ion concentration is independent of salt concentration. The hydroxyl ion concentration increases with time and was assumed to be one-half of the faradays passed for a time average. The correction varied from 0.024 to 0.002 compared with a normal Hittorf error of ~0.010 (2%).

The data used to calculate the transference numbers at various salt concentrations in water at 25° are recorded in Table 1. The corrected transference numbers agree well with literature values[7] and the agreement is well within the experimental error of the Hittorf method.

TABLE 1

HITTORF TRANSFERENCE NUMBERS FOR THE IONS OF LiCl IN WATER AT 25°

| *Concn. LiCl (moles per 1000 g soln.)* | $Ag_1$ | $Ag_2$ | $F \cdot 10^3$ | $t_c$ | $t_a$ | $W$ |
|---|---|---|---|---|---|---|
| 0.0959 | 0.86752 | 0.86720 | 8.04 | 0.314 | 0.686 | 211.3700 |
| 0.0959 | 0.85882 | 0.86437 | 8.01 | 0.307 | 0.693 | 210.5873 |
| 0.0970 | 0.64722 | 0.64709 | 6.50 | 0.314 | 0.686 | 210.0421 |
| 0.193 | 0.72252 | 0.72257 | 6.70 | 0.296 | 0.704 | 209.7471 |
| 0.212 | 0.89155 | 0.89163 | 8.26 | 0.314 | 0.686 | 211.2094 |
| 0.212 | 0.85665 | 0.85659 | 7.94 | 0.300 | 0.700 | 208.1092 |
| 0.289 | 0.75506 | 0.75576 | 7.00 | 0.283 | 0.717 | 210.2320 |
| 0.289 | 0.78437 | 0.78430 | 7.27 | 0.300 | 0.700 | 211.5258 |
| 0.290 | 0.85493 | 0.85426 | 7.92 | 0.319 | 0.681 | 211.2494 |
| 0.483 | 0.87089 | 0.86803 | 8.06 | 0.300 | 0.700 | 208.0326 |
| 0.577 | 0.59300 | 0.59291 | 5.50 | 0.300 | 0.700 | 213.0012 |
| 0.596 | 0.87216 | 0.87425 | 8.09 | 0.295 | 0.705 | 213.3093 |
| 0.596 | 0.86428 | 0.86429 | 8.01 | 0.301 | 0.699 | 213.0237 |
| 0.891 | 0.84852 | 0.84920 | 7.87 | 0.287 | 0.713 | 214.8903 |

In Fig. 1, $\Delta G^F_{\mathrm{sol}}$ is plotted against the concentration of lithium chloride. The values at 0.1 and 1.0 moles per 1000 g of solution were calculated from ULICH's values[8] for total solvation of lithium chloride assuming that the ratio of lithium ion

TABLE 2

HITTORF TRANSFERENCE NUMBERS AND GRAMS OF SOLVENT TRANSPORTED FROM THE ANODE TO THE CATHODE FOR LiCl AT 25°

| *Dioxane* (%) | *Concn. LiCl* (*moles per 1000 g soln.*) | $\alpha_m$ | $\alpha_a$ | $Ag_1$ | $Ag_2$ | $F \cdot 10^3$ | $W$ | $C_a$ | $t_c$ | $t_a$ | $d_m$ | $d_a$ | $\Delta G^F_{sol}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.0 | 0.1930 | 10.399 | 10.416 | 0.72252 | 0.72257 | 6.70 | 209.7471 | — | 0.285 | 0.715 | 1.00849 | 1.00836 | 42.1 |
| 0.0 | 0.2120 | 11.848 | 11.854 | 0.89155 | 0.89163 | 8.26 | 211.2094 | — | 0.302 | 0.698 | 1.00622 | 1.00488 | 34.0 |
| 15.1 | 0.1937 | 10.494 | 10.475 | 0.99380 | 0.99343 | 9.21 | 214.1482 | 0.179 | 0.351 | 0.649 | 1.02170 | 1.02163 | −55.4 |
| 15.1 | 0.1937 | 10.494 | 10.484 | 0.83215 | 0.83207 | 7.71 | 213.6707 | 0.182 | 0.333 | 0.667 | 1.02170 | 1.02144 | −33.6 |
| 30.0 | 0.1937 | 12.757 | 12.783 | 0.80538 | 0.80505 | 7.46 | 215.2210 | 0.183 | 0.319 | 0.681 | 1.03298 | 1.03276 | 41.3 |
| 30.0 | 0.1932 | 10.335 | 10.358 | 0.90709 | 0.90667 | 8.41 | 209.9743 | 0.181 | 0.305 | 0.695 | 1.03292 | 1.03282 | 45.3 |
| 45.9 | 0.1916 | 10.696 | 10.719 | 0.87900 | 0.89388 | 8.22 | 215.2091 | 0.180 | 0.318 | 0.682 | 1.04305 | 1.04267 | 52.4 |
| 45.9 | 0.1916 | — | — | 0.83218 | 0.83187 | 7.71 | 215.3808 | 0.179 | 0.366 | 0.757 | — | — | — |
| 45.9 | 0.1928 | 25.729 | 25.781 | 0.85880 | 0.85917 | 7.96 | 216.3208 | 0.180 | 0.358 | 0.642 | 1.04289 | 1.04259 | 37.9 |
| 60.5 | 0.1866 | — | — | 0.99061 | 0.99060 | 9.182 | 217.2903 | 0.176 | 0.243 | 0.634 | — | — | — |
| 60.5 | 0.1866 | 10.441 | 10.486 | 1.00225 | 1.00331 | 9.295 | 220.1646 | 0.175 | 0.277 | 0.723 | 1.04747 | 1.04782 | 82.4 |
| 60.5 | 0.1923 | 12.967 | 13.032 | 0.80992 | 0.80939 | 7.50 | 217.0692 | 0.183 | 0.262 | 0.738 | 1.04773 | 1.04757 | 138.4 |
| 84.1 | 0.1870 | 10.701 | 10.757 | 0.31869 | 0.32742 | 2.99 | 218.1051 | 0.184 | 0.223 | 0.777 | 1.04512 | 1.04522 | 365.0 |
| 84.1 | 0.1870 | 10.701 | 10.753 | 0.34094 | 0.33980 | 3.16 | 219.2748 | 0.184 | 0.213 | 0.787 | 1.04512 | 1.04529 | 318.2 |

solvation to chloride ion solvation is 14 : 4. The value at 1.3 moles per 1000 g of solution has been reported by MACINNES[9], and that at 0.4 moles per 1000 g of solution by WEAR *et al.*[3]. The data for approximately 0.2 moles per 1000 g of solution are recorded in Table 2. Figure 1 is a typical solvation curve showing a decrease in solvation with an increase in concentration. The levelling off is due to the attainment of a minimum solvation that is independent of concentration.

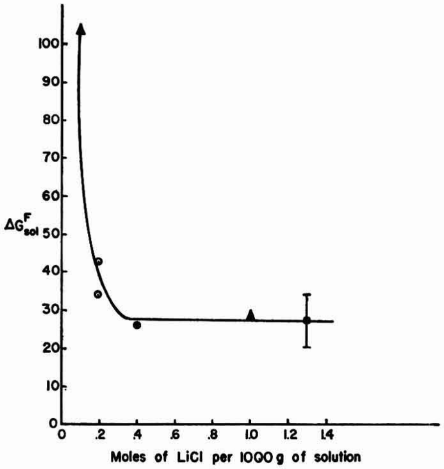

Fig. 1. Grams of solvent transported from anode to cathode per faraday of electricity plotted against moles LiCl per 1000 g of solution in aqueous soln. at 25°: (○), this investigation; (▲), ULICH; (●), WEAR *et al.*; (■), MACINNES.

The data for Figs. 2 and 3 are recorded in Table 2. Figures 2 and 3 are plots of

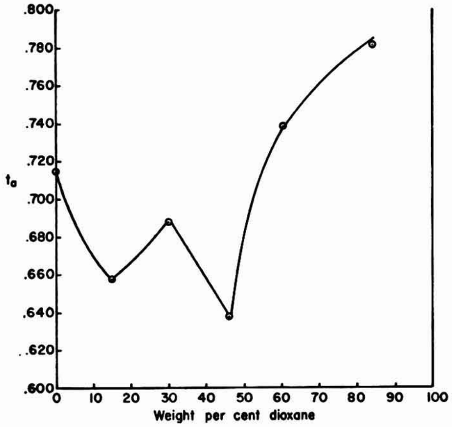

Fig. 2. Anion transference number at 0.19 moles LiCl per 1000 g of solution plotted against weight per cent dioxane in solvent at 25°.

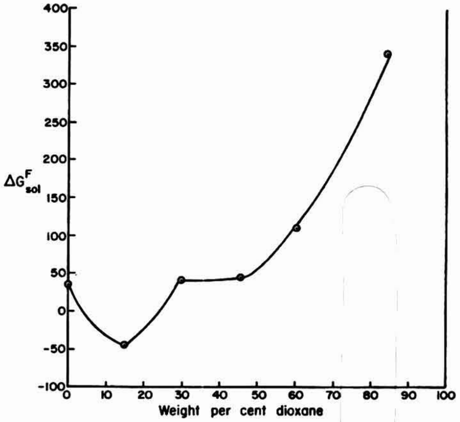

Fig. 3. Calculated grams of solvent transferred from anode to cathode per faraday of electricity at 0.19 moles LiCl per 1000 g of solvent plotted against weight per cent dioxane in solvent at 25°.

$t_a$ and $\Delta G_{\text{sol}}^{F}$, respectively, against the percentage weight of dioxane in the solvent at 0.19 moles of lithium chloride per 1000 g of solution. To interpret this data to the fullest advantage, Figs. 2 and 3 must be considered together because the transference number is dependent on the bulk of the ion and the solvation determines any bulk above that of the stripped ion.

As the concentration of dioxane increases from zero to 15% by weight, both $t_a$ and $\Delta G_{\text{sol}}^{F}$ decrease. If the dioxane molecules begin to break up the structure of water, the outer solvation layers of the ions will cease to exist because the outer solvation sheaths are primarily held by the structure of water. This dehydration effect will take more water from the lithium ion than the chloride ion and consequently, the chloride ion will be relatively more bulky. This will cause both $t_a$ and $\Delta G_{\text{sol}}^{F}$ to decrease.

Between 15% and 30% by weight of dioxane, both $t_a$ and $\Delta G_{\text{sol}}^{F}$ increase. This can be explained by the chloride ion losing water of solvation causing $t_a$ to increase because of a less bulky chloride ion; $\Delta G_{\text{sol}}^{F}$ would also increase since less solvent would be carried to the anode compartment.

Between 30% and 45% by weight of dioxane $\Delta G_{\text{sol}}^{F}$ remains constant within experimental error, but $t_a$ decreases. Both the lithium and chloride ions lose additional water of solvation, but in such a way that $t_a$ decreases. The change in solvation and transference numbers is such that $\Delta G_{\text{sol}}^{F}$ remains constant at a value depending on the product of these two values as shown in the following equation:

$$\Delta G_{\text{sol}}^{F} = G_{\text{sol}}^{\text{Li}} t_c - G_{\text{sol}}^{\text{Cl}} t_a \tag{4}$$

Between 45% and 84% by weight of dioxane both $t_a$ and $\Delta G_{\text{sol}}^{F}$ increase. This is easily explained if the lithium ion becomes solvated with more and more dioxane in place of water. This increase in dioxane solvation will make the lithium ion more bulky and therefore slow it down, but the mass added to the solvent sheaths is enough to more than overcome the decrease of $t_c$. The formation of ion triples would also cause a decrease in $t_c$.

This type of explanation for the curves in Figs. 2 and 3 seems to be the best possible explanation as it has been used successfully with the previous systems[1-5].

A comparison of the present system with the lithium chloride in water–ethanol solvents shows that the results of the two systems are quite different. In water–ethanol solvents $t_a$ has little if any dependence on the concentration of ethanol, but varies considerably with the dioxane concentration. In the water–ethanol system a plot of $\Delta G_{\text{sol}}^{F}$ against percentage weight of ethanol gives a sine-like curve with increasing amplitude and frequency as the ethanol concentration is increased. Figure 3 does not show much resemblance to the water–ethanol curve. The reason for these differences is probably due to the fact that ethanol, being similar to water, has little effect on the water structure; dioxane, however, is very different from water and breaks up the water structure.

## ACCURACY AND PRECISION

Inspection of the anion transference numbers at equal salt concentrations in Tables 1 and 2 gives the average deviation from the average value for $t_a$ as ±1.3% which is within the 2% accuracy of the method. The average deviation from the average value for $\Delta G_{\text{sol}}^{F}$ from the figures at equal salt concentrations in Table 2 is ±13%.

## APPENDIX

Definitions, not given in the text, of symbols used are as follows:

| | |
|---|---|
| $p_s^a$, $p_s^m$ | per cent by weight of lithium chloride in the anode and middle compartment solutions, respectively, |
| $W$ | total mass in grams of the solution in the anode, |
| $A_{\mathrm{Ag}}$ | gram ionic weight of the silver ion, |
| $W_{\mathrm{Ag}}$ | weight of silver deposited in the coulometer, |
| $\lambda_c$, $\lambda_a$ | equivalent conductances of cation and anion, respectively, |
| $t_{\mathrm{OH}^-}$ | transference number of the hydroxyl ion, |
| $\Delta G^F_{\mathrm{sol}}$ | grams of solvent transferred from anode to cathode per faraday of electricity, |
| $\alpha_a$, $\alpha_m$ | measured angular rotations at 25° of the solutions from the anode and middle compartments, respectively, |
| $d_a$, $d_m$ | respective densities of the anode and middle compartment solutions, |
| $f_s^a$, $f_s^m$ | respective fractions of the solutions that are lithium chloride in the anode and middle compartments, |
| $F$ | number of faradays of electricity passed through the solution. |

## ACKNOWLEDGEMENTS

The authors thank the Atomic Energy Commission for Contract AT-(40-L)-2069 which financially supported this research.

## SUMMARY

Transference and solvation phenomena for the ions of lithium chloride in water and water–dioxane solvents have been studied. The transference numbers of the anion as a function of salt concentration in water and as a function of solvent composition are presented graphically and discussed in relation to relative solvation of the lithium and chloride ions. The amount of solvent transferred from the anode to the cathode is presented graphically and discussed.

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# A PRELIMINARY INVESTIGATION ON DERIVATIVE CYCLIC CONSTANT CURRENT VOLTAMMETRY

PETER E. STURROCK

*School of Chemistry, Georgia Institute of Technology, Atlanta, Ga. (U.S.A.)*

(Received July 24th 1964)

## INTRODUCTION

A new electroanalytical method, Derivative Cyclic Constant Current Voltammetry (DCCCV), has been developed in this laboratory. The equipment, experimental technique, and preliminary results are reported in this article. The method is basically an extension of cyclic chronopotentiometry as described by HERMAN AND BARD[1-3], but has many similarities to the oscillographic polarography with alternating current developed by HEYROVSKÝ AND FOREJT[4]. In DCCCV, as in cyclic chronopotentiometry, a constant current is passed through an electrolysis cell and reversed at preset values of the test electrode potential. Thus the potential of the working electrode scans back and forth between the chosen limits under the influence of a constant current. Instead of displaying the electrode potential, $E$, *vs.* time, $t$, as is done in chronopotentiometry, the time derivative of electrode potential, $dE/dt$, is presented *vs.* $E$ as is done in oscillographic polarography with alternating current. Thus the display is very similar in appearance to that of the HEYROVSKÝ–FOREJT (H–F) method, but the experimental conditions are quite different and the new method has some advantages over the H–F method.

Consider the current reversal chronopotentiogram shown in Fig. 1(a). As the potential of the working electrode rises rapidly at first, its derivative with respect to time is also large and positive. Then as the potential plateau is reached, the derivative decreases and theoretically should go to zero at the $E_{\frac{1}{4}}$ point before increasing again toward the end of the transition. After the current is reversed the derivative will be large, but negative. Again it will approach zero as the $E_{\frac{1}{4}}$ point is approached and then become more negative (see Fig. 1(b)) towards the end of the transition. The time between peaks on the derivative curve can be used to measure transition times as suggested by IWAMOTO[5].

If the derivative is displayed against the electrode potential, Fig. 1(c) is obtained. If the electrode process is reversible, the potentials at the minima in the cathodic and anodic derivative curves should coincide. The depth of the incision depends upon several factors including the current density, depolarizer concentration, and the time constant of the differentiator. The incision depth can be used for quantitative analysis and the potential at which the incision occurs for qualitative analysis.

While DCCCV may serve for all of the applications of the H–F method, it differs in several respects. In the H–F method a sine wave current is passed through the cell at a frequency determined by the current source. The magnitude of voltage change during one cycle is dependent upon the average current density and the solution composition. In DCCCV, the current is held constant although its direction is reversed midway in the cycle. From one experiment to another the potential range and current magnitude can be independently varied. The frequency of the cycle then depends upon the electrode area and the solution composition.

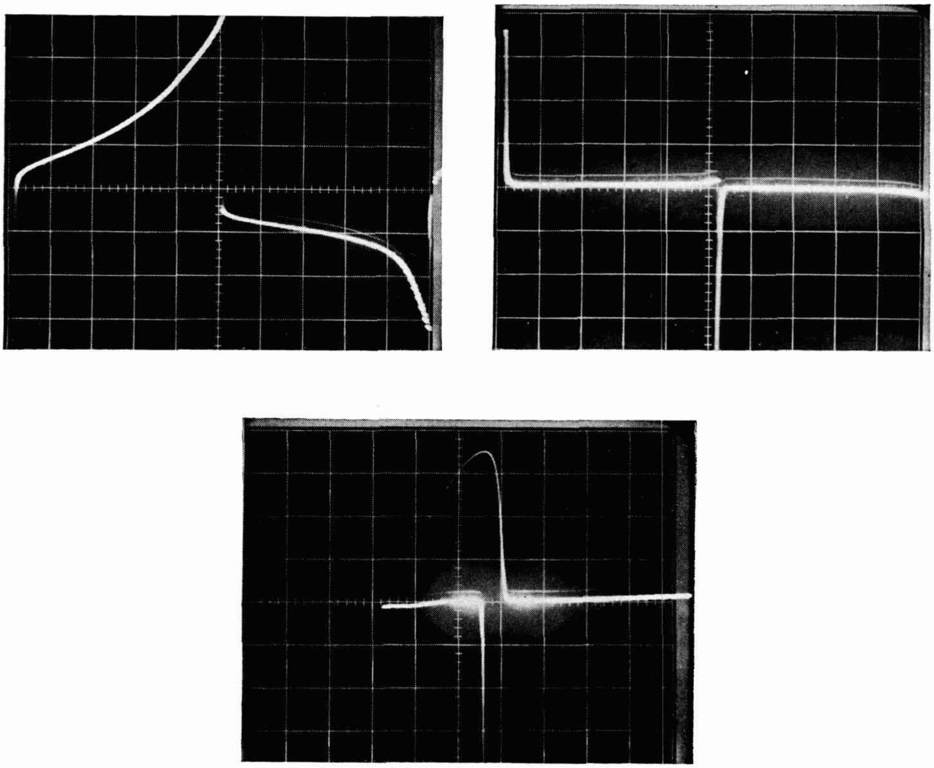

Fig. 1. Comparison of chronopotentiometry to DCCCV system: $1.0 \cdot 10^{-3}$ *F* $CdCl_2$ in $1.0 \cdot 10^{-1}$ *F* KCl. Electrode, hanging mercury drop; current density, 670 $\mu$A /cm$^2$. (a) Current reversal chronopotentiogram (after cycling until transition times are constant). X axis, 0.2 sec/div.; Y axis, $-0.2 - -1.0$ V *vs.* S.C.E. (b) Derivative of (a). Differentiator settings, R = 10 M$\Omega$, C = 0.1 $\mu$F; X axis, 0.2 sec/div.; Y axis, d*E*/d*t*, 10 V/div. (c) DCCCV of (a). Differentiator settings, R = 10 M$\Omega$, C = 0.1 $\mu$F; X axis, $0 - -1.0$ V *vs.* S.C.E.; Y axis, d*E*/d*t*, 10 V /div.

In the H–F method the cell voltage and its time derivative are measured. In DCCCV a three electrode system is used so that the potential of the working electrode and its time derivative are measured essentially free of the *IR* drop and counter electrode polarization which complicate the situation in the H–F method. Thus the techniques for *IR* correction commonly used with the H–F method are not necessary.

An additional benefit of the three electrode system is that a lower concentration of supporting electrolyte may be used than in the H–F method and thus the problem of trace impurities in the supporting electrolyte is decreased. Supporting electrolyte concentrations of less than 0.01 *F* are seldom used in the H–F method while excellent results can be obtained in DCCCV with a $1.0 \cdot 10^{-4}$ *F* supporting electrolyte. In the latter case the supporting electrolyte is needed only to minimize migration current in quantitative analysis and to lower the ohmic resistance of the solution, so that the applied voltage required for the desired current is within the output capability of the galvanostat amplifier. This means that an *IR* drop of 50–100 V between the working and counter electrodes can be tolerated.

## INSTRUMENT

The multipurpose instrument built in this laboratory can be used for conventional, current reversal, and cyclic chronopotentiometry with either a two electrode or three electrode cell as well as for the derivative method discussed in this paper. Switches are provided so that the initial current can be selected as either anodic or cathodic when the instrument is changed from standby to cell. Furthermore, it is possible to select independently the magnitudes of the anodic and cathodic currents. In addition the instrument serves as a versatile function generator for square, triangular, and saw-tooth waves with a follower output.

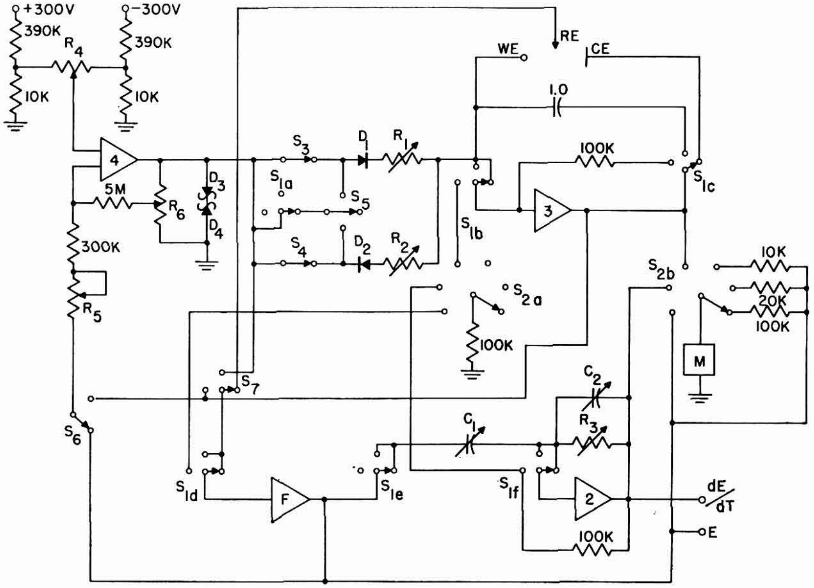

Fig. 2. Schematic diagram. $C_1$, 0.01, 0.1, 1.0 $\mu$F; $C_2$, 10 pF – 0.004 $\mu$F in 5 steps; $D_1$,$D_2$, silicon signal diodes, 1 N 457 A; $D_3$, $D_4$, matched Zener diodes, 1 N 1771; $R_1$, $R_2$, 5 k$\Omega$ – 20 M$\Omega$ in 11 steps (1% tolerance); $R_3$, 10 k$\Omega$ – 25 M$\Omega$ in 4 steps; $R_4$, 100 k$\Omega$, 10 turn; $R_5$, 100 k$\Omega$; $R_6$, 10 k$\Omega$, 10 turn; $S_1$, 6 pole, 3 position, shorting, rotary; $S_2$, 2 pole 6 position, rotary.

The instrument was built into a chassis (Plug-in Module Heathkit EUA 19-1) and is used with a Heathkit EUW 19-A operational amplifier chassis. The display is presented on either an oscilloscope (Tektronix 561-A with C-12 camera) or an X–Y recorder (Houston Instrument Co. HR-96T).

The circuit, Fig. 2, was developed from that of a function generator built in this laboratory which in turn embodies many ideas from SHAIN[6] and ENKE[7]. Amplifier No. 4 is a flip-flop whose output is clipped to a symmetrical square wave by a pair of matched 10 V Zener diodes. The flip-flop may be triggered from either the output of amplifier No. 3 or the follower amplifier. The No. 3 amplifier is the galvanostat and holds the working electrode at virtual ground. When $S_1$ is in the standby position a 1.0 $\mu$F capacitor is connected across amplifier No. 3, which then functions as an integrator and generates a triangular wave from the square wave. A triangular wave can also be generated by connecting a capacitor across the jacks for the working electrode and counter electrode and setting $S_1$ in the operate position.

The follower amplifier can be switched to the square wave output, the reference electrode or the counter electrode. Amplifier No. 2 serves as the differentiator with $C_1$, $C_2$, and $R_3$ ganged together on one switch to give 12 R–C combinations.

The span control, $R_6$, can adjust the potential range from 2 V to about 0.03 V. The center of span control, $R_4$, can adjust the span midpoint from $+2.2$V–$-4.8$ V with regard to the reference or counter electrode potential.

The diodes, $D_1$ and $D_2$, and current regulating resistances, $R_1$ and $R_2$, allow independent regulation of the anodic and cathodic currents and also the generation of unsymmetrical triangular waves. The component resistors of $R_1$ and $R_2$ have a 1% tolerance. When $S_4$ is opened, no cathodic current will flow and therefore the instrument will go to the anodic extreme, trigger the flip-flop, and then hold at that point. Likewise $S_3$ can be used to halt the sweep at its cathodic extreme. If a single cathodic sweep is desired, the cycle is halted by opening $S_4$; then $S_3$ is opened and $S_4$ closed. For a single anodic sweep the switching sequence is reversed.

Switch $S_5$ can short out either $S_3$ or $S_4$ when $S_1$ is in the operate position. If it is desired to obtain a cyclic chronopotentiogram with the cycle starting on a cathodic sweep, the following switching sequence is used. Set $S_5$ so that it will short out $S_4$ when the cell is connected. With $S_1$ in the standby position, halt the sweep at the anodic extreme by opening $S_4$ and then connect the cell by switching $S_1$ to the operate position. If $S_3$ is used instead of $S_4$ the cycle can be started on an anodic sweep. With $S_1$ in the first position, $S_2$ can switch the 50-0-50 $\mu$A meter directly to the outputs of amplifiers Nos. 1, 2, or 3 for adjusting the bias. The last three positions of $S_2$ give meter ranges of $\pm 0.5$, $\pm 1$, and $\pm 5$ V in the follower output.

## EXPERIMENTAL

All experiments were performed in 100 ml Berzelius beakers. The electrodes and $N_2$ bubbler were inserted through a rubber stopper. Enough mercury was poured into the beaker to cover the bottom and electrical connection to this counter electrode was made with a platinum wire sealed into a glass tube. The dropping mercury electrode had a capillary characteristic of 1.97 $mg^{\frac{2}{3}}$ $sec^{-\frac{1}{2}}$. For experiments with a hanging drop electrode a glass spoon was used to catch one or more drops from the D.M.E. and to hang them on a mercury plated platinum wire sealed into a glass tube. The calomel reference electrode was a Beckman No. 39170 fibre junction electrode equipped with a shielded lead.

All chemicals were reagent grade. Solutions were prepared in 50 ml volumetric flasks and then poured into the cell and outgassed with nitrogen for at least ten minutes.

The usual procedure was to calibrate the X axis of the oscilloscope for the desired potential range and then to set the instrument span and center of span controls while observing the tracing on the oscilloscope. Then the instrument was switched to standby, the hanging drop replaced with a fresh one, and the photograph taken after switching back to the cell.

## RESULTS AND DISCUSSION

The following results are reported to show various applications of DCCCV. Work is continuing in this laboratory and significant improvements in instrumentation (especially in the cell switching circuit) and technique are anticipated.

### *Qualitative analysis*

Several oscillograms are shown in Fig. 3. The cathodic minima for lead, cadmium,

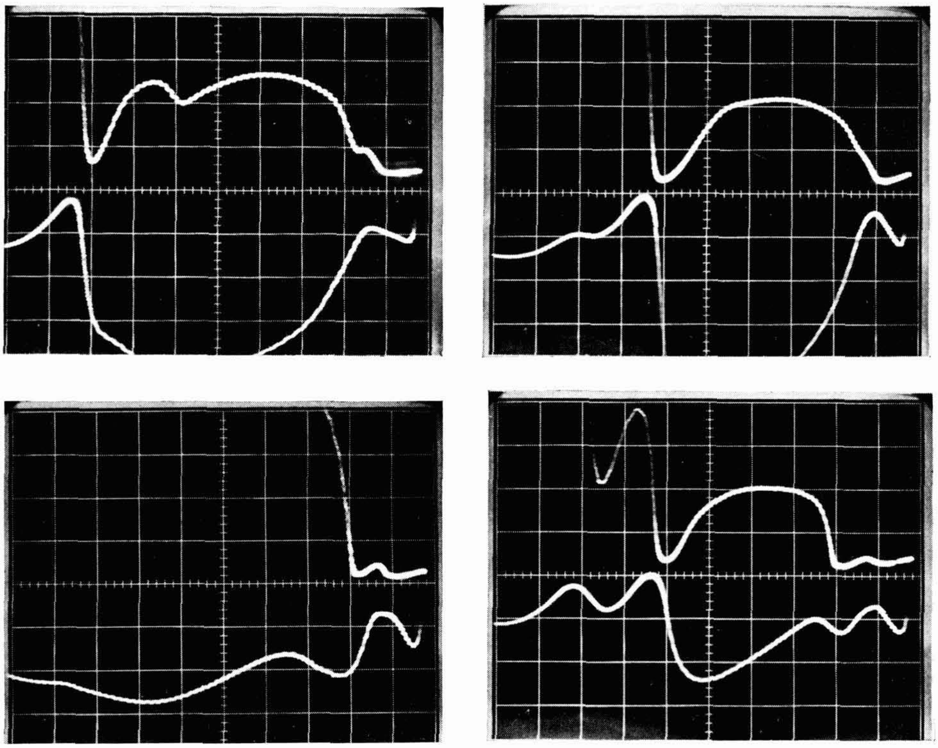

Fig. 3. DCCCV oscillograms of lead, cadmium, and zinc. Supporting electrolyte, $1.0 \cdot 10^{-3}$ *F* KCl; electrode, hanging mercury drop; current density, 16.7 $\mu$A/cm$^2$; differentiator settings, R = 25 MΩ, C= 1.0 $\mu$F; X axis, $-0.2$ – $-1.2$ V *vs.* S.C.E.; Y axis, d*E*/d*t*, 10 V/div. (a) $1.0 \cdot 10^{-5}$ *F* $PbCl_2$; (b) $1.0 \cdot 10^{-5}$ *F* $CdCl_2$; (c) $1.0 \cdot 10^{-5}$ *F* $ZnCl_2$; (d) $1.0 \cdot 10^{-5}$ *F* in each, $PbCl_2$, $CdCl_2$, $ZnCl_2$.

and zinc occur at −0.40, −0.60, and −1.03 V *vs.* S.C.E., respectively, and thus agree well with the usual polarographic half-wave potentials or the chronopotentiometric quarter transition time potentials.

Figure 4 shows the effect of current density on a reversible process. The solution and electrode are the same as used to obtain Fig. 3(b), but the settings of the differentiator and oscilloscope's vertical gain are different for each oscillogram, hence a comparison of incision depth is meaningless. However, it should be noted that the incision potentials are shifted with increased current density and that the sharpness of the incision decreases. Thus the resolution and identification of a multicomponent system is enhanced with lower current density. (See Fig. 3(d).)

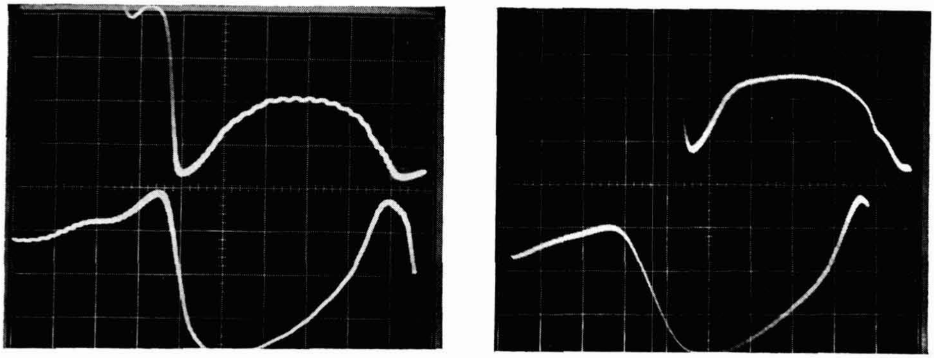

Fig. 4. Effect of current density. System, $1.0 \cdot 10^{-5}$ *F* $CdCl_2$ in $1.0 \cdot 10^{-3}$ *F* KCl; electrode, hanging mercury drop; X axis, −0.2 – −1.2 V *vs.* S.C.E. (a) Differentiator settings, R = 10 MΩ, C = 1.0 μF; current density, 33.4 μ A/cm²; Y axis: d*E*/d*t*, 10 V/div. (b) Differentiator settings, R = 25 kΩ, C = 1.0 μF; current density, 167 μA/cm²; Y axis, d*E*/d*t*, 0.1 V/div.

*Quantitative analysis*

Quantitative analysis must be performed by reference to a calibration curve obtained under the same experimental conditions as the unknown. Figure 5 shows such a calibration curve for cadmium. In this case the current was allowed to cycle for five minutes before the distance between the zero axis (d*E*/d*t* axis) and the incision minimum was measured. Since this measurement should be inversely proportional to transition time and therefore inversely proportional to the square of the concentration, it was expected that a plot of pCd *vs.* the logarithm of the incision height would be linear. This was approximately true for lower concentrations, but a pronounced curvature was found at higher concentrations. Attempts to improve the linearity by taking into account the background-charging curve were unsuccessful.

Unfortunately, quantitative analysis of mixtures by DCCCV does not appear feasible. The problem has long been recognized in the chronopotentiometry of mixtures[3,5,8]. In brief, the difficulty is that the apparent cathodic transition time of a substance is increased by the presence of a second substance reducible at a more positive potential. Likewise, the apparent anodic transition time is increased by the presence of a second substance oxidizable at a more negative potential. Therefore, in the preparation of the calibration curve, it would be necessary to maintain the con-

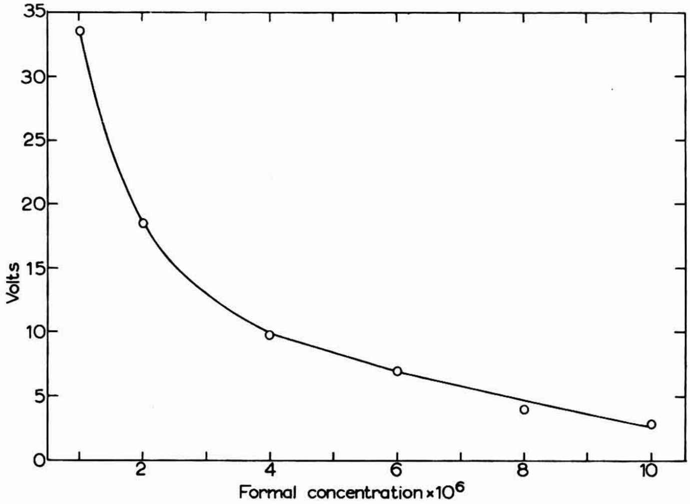

Fig. 5. Calibration curve for cadmium. Supporting electrolyte, 1.0 · $10^{-3}$ $F$ KCl; electrode, hanging mercury drop; current density, 16.7 $\mu$A/cm$^2$; differentiator settings, R = 25 MΩ, C = 1.0 $\mu$F. Y axis, d$E$/d$t$ at cathodic minimum of DCCCV oscillograms expressed in volts.

centrations of all other electroactive substances exactly as in the unknown. In addition, surface active agents affect the curves and must be kept at the same level.

### *Trace analysis*

As in several other electroanalytical methods, it is possible to examine very dilute solutions of amalgam-forming substances by first concentrating the substance in the

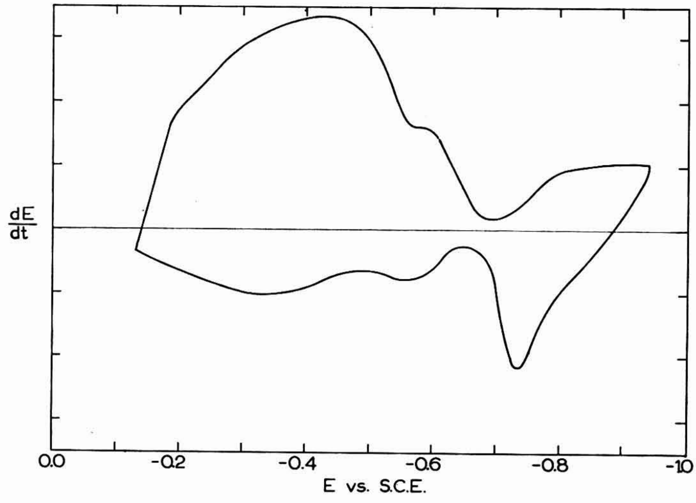

Fig. 6. DCCCV curve of cadmium after preelectrolysis. System, 1.0 · $10^{-7}$ $F$ CdCl$_2$ in 1.0 · $10^{-4}$ $F$ KCl; electrode, hanging mercury drop; current density, 5.6 $\mu$A/cm$^2$; differentiator settings, R = 2.5 MΩ, C = 1.0 $\mu$F; Y axis, d$E$/d$t$, 5 V/div. Preelectrolysis, 15 min at −0.8 V *vs.* S.C.E.

electrode drop by a preelectrolysis. A sizeable incision is then obtained on the d$E$/d$t$ curve when the current is cycled.

Figure 6 shows the result of applying this technique to a solution $1.0 \cdot 10^{-7}$ $F$ in $CdCl_2$ and $1.0 \cdot 10^{-4}$ $F$ in KCl. Five drops of mercury were collected from the D.M.E. and hung together as the working electrode. Then the solution was preelectrolyzed for fifteen minutes at −0.80 V *vs.* S.C.E. with stirring provided by bubbling $N_2$; then a current of 0.5 μA was cycled. The readout was obtained in this case on the X–Y recorder with the X axis calibrated for 0 to −1.0 V and the Y axis at 5 V/div.

This does not by any means represent the lower limit of sensitivity of the method since only a short preelectrolysis with inefficient stirring was used. However, extension to lower concentrations will require the usual precautions against adsorption of the substance on the walls of the container.

*Differential capacitance studies*

The differential capacitance and related adsorption phenomena can readily be studied by DCCCV. In a recent article, ANGERSTEIN-KOZLOWSKA AND CONWAY[9] pointed out that the derivative galvanostatic approach has an advantage over other methods in that the capacitance can be worked out in terms of steady-current kinetics. In some cases the display of d$E$/d$t$ *vs.* $E$, as obtained in DCCCV, is more useful than the d$E$/d$t$ *vs.* $t$ display used in ref. 9.

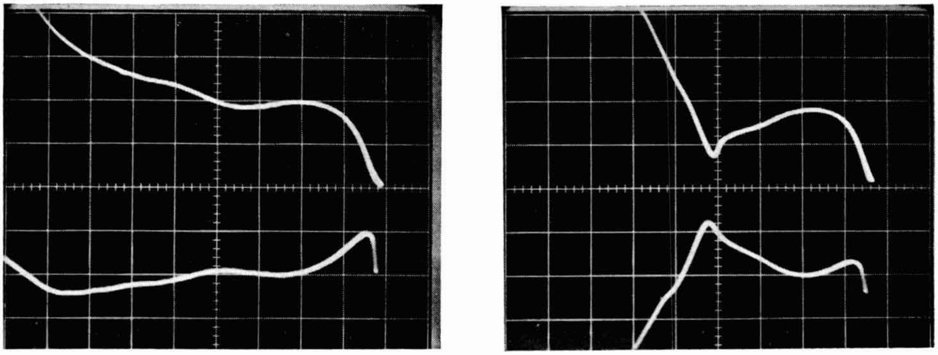

Fig. 7. Capacitance charging curves. Electrode, hanging mercury drop; current density, 1.67 mA/cm²; differentiator settings, R= 25 kΩ, C= 1.0 μF; X axis, −1.0 – −2.0 V *vs.* S.C.E.; Y axis, d$E$/d$t$, 1 V/div. (a) 1.0 $F$ KOH; (b) 2 v/v% pyridine in 1.0 $F$ KOH.

Figure 7 shows the charging curves for 1.0 $F$ KOH and 2.0 v/v % pyridine in 1.0 $F$ KOH. The anodic portions of the oscillograms show the usual differential capacitance curve up to about −1.8 V *vs.* S.C.E. where the start of the hydrogen wave can be seen. If it is desired to look at the cathodic curve in its usual form it is only necessary to reverse the connections to the vertical plates of the oscilloscope or to reverse the Y axis input leads of the X–Y recorder. For a quantitative estimate of the capacitance it is only necessary to make a calibration curve using several precision capacitors consecutively in place of the cell, and with no changes in the settings of the current, differentiator, and oscilloscope's vertical gain.

## FUTURE WORK

Work, planned or in progress in this laboratory, includes investigations with other electrodes such as platinum, carbon paste, pyrolytic graphite, streaming mercury, and dropping mercury. For the dropping mercury electrode it will be necessary to use an interrupter circuit so that scanning occurs only during a brief and reproducible portion of the drop life.

Another area of investigation will be the use of modified DCCCV to detect a titration endpoint. For this purpose a display of log $\mathrm{d}E/\mathrm{d}t$ *vs.* $E$ will be used.

A third general area of investigation will be with non-aqueous solvents. Here the tolerance of DCCCV to high solution resistance should prove advantageous.

## SUMMARY

A new electroanalytical method, Derivative Cyclic Constant Current Voltammetry (DCCCV), has been described. Its application to qualitative and quantitative analysis as well as to investigations of differential double layer capacitance has been discussed.

A multipurpose instrument utilizing operational amplifiers has been described. The instrument can be used for conventional, current reversal, and cyclic chronopotentiometry as well as for the new method. In addition, the instrument can serve as a generator of square, triangular, and saw-tooth waves.

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# NICKEL(IV) DIMETHYLGLYOXIME

DONALD G. DAVIS AND EDWARD A. BOUDREAUX

*Department of Chemistry, Louisiana State University in New Orleans, New Orleans, La. (U.S.A.)*

(Received July 24th, 1964)

## INTRODUCTION

For many years the reaction of nickel(II) dimethylglyoxime with an oxidizing agent in strong base to form a deep red color[1,2] has been of use to analytical chemists both for spot tests and for colorimetric analysis. There has, however, been considerable disagreement in the literature as to the structure and form of the red colored material. Some of the proposals include $DH_2Ni(IV)O$[1], $Ni(III)DH_2OH$[3], $Ni(IV)DH_2^{ox}$[4], $Ni(IV)D_3^{2-}$[5,6], and an oxygen carrying chelate of unknown structure[7]. (For the sake of convenience dimethylglyoxime will be represented by $DH_2$. $DH_2^{ox}$ stands for an oxidized form of dimethylglyoxime, probably furoxane.) In view of the possibility of the red material being an oxygen carrying chelate, it was decided that an electrochemical study to examine the reduction of oxygen attached to the metal chelate would be of interest. Polarography, chronopotentiometry and controlled potential electrolysis were found to be of use. Magnetic susceptibility and spectrophotometry were also applied to this study. The results of this work, however, indicate that the red complex contains nickel in the +4 oxidation state and that all the evidence considered to support the idea of an oxygen carrying chelate can be explained in these terms.

## EXPERIMENTAL

All chemicals used in this study were reagent grade and used without further purification. Solutions of dimethylglyoxime in 1.5 *M* sodium hydroxide were prepared fresh weekly. A nickel(II) nitrate stock solution was standardized by titration with EDTA.

Polarograms were recorded using a Sargent Model XV polarograph and a dropping mercury electrode for which $m = 1.10$ mg/sec and $t = 7.10$ sec when $h = 29.8$ cm and $E = -0.40$ V *vs.* the saturated calomel electrode. All experiments were carried out at $25.0 \pm 0.1°$. When desirable, solutions were deaerated by a rapid stream of nitrogen from which traces of oxygen were removed by a vanadous chloride scrubber.

Controlled potential electrolysis experiments were carried out using an Analytical Instruments potentiostat and current integrator. The working electrode was of platinum gauze or mercury. The cell construction for the platinum electrode has been previously described[8]. The cell used with the mercury electrode was that supplied with the potentiostat. The values at which the electrode potential was controlled were selected by viewing polarograms or, in the case of the platinum electrode, chronopotentiograms taken at a shield platinum electrode in the usual manner[9].

Visible and u.v. adsorption spectra were recorded using either a Beckman DB or a DK-1 spectrophotometer.

Magnetic susceptibility measurements were made employing the standard Gouy technique. The apparatus consisted of a Mettler single pan semi-micro balance, electromagnet, double end sample tube and heating coil for elevated temperature control. Measurements were made on solutions 0.002 $M$ in $Ni(NO_3)_2$, 0.0095 $M$ in dimethylglyoxime and 1.5 $M$ in NaOH at a field strength of 6500 gauss, and five different temperatures within the range 299°–340°K.

Since the measured weight differences were small, control measurements were run concurrently on solutions containing all components except nickel and on a solution containing only $Ni(NO_3)_2$, to ensure that the observed changes were due only to complexation. Assuming the validity of the additivity law, the susceptibility of the complex was computed from the observed susceptibility differences between the complex and control solutions for which the concentrations of all constituents were known. The minimum accuracy in these determinations was established to be 1%. Data were taken both on solutions saturated with nitrogen and on solutions saturated with oxygen.

## RESULTS AND DISCUSSION

*Polarography* The red oxidized complex may be formed by dissolving solid nickel(II) dimethylglyoxime in a solution of sodium hydroxide and allowing oxygen from the air to contact the solution. This is a slow process, however, and solutions are better prepared by adding a measured amount of nickel(II) solution to a dimethylglyoxime–sodium hydroxide solution. Immediately upon the addition of nickel(II), a yellow color forms—$Ni(OH)_2$ forms first but rapidly dissolves. If all the solution components are kept air free and no oxidizing agents were added, the reaction stops at this point. An absorption peak at 380 m$\mu$ was observed for such a solution. If the nickel dimethylglyoxime–sodium hydroxide solution was allowed to stand in contact with air (or treated with an oxidizing agent such as $PbO_2$), the solution gradually became dark red. (Absorption maximum 470 m$\mu$.)

By mixing various amounts of nickel and dimethylglyoxime in 1.5 $M$ sodium hydroxide it was found that a ratio of at least three moles of dimethylglyoxime per mole of nickel was necessary for maximum color intensity (and maximum diffusion current). A series of polarograms was then recorded with varying nickel concentrations between $0.05 \cdot 10^{-3}$ and $1 \cdot 10^{-3}$ $M$. The concentration of dimethylglyoxime was $5 \cdot 10^{-3}$ $M$, and of sodium hydroxide 1.5 $M$. Various methods of oxidizing the solution to the red material were tried. The most precise results were obtained by treating the solution with a small amount of $PbO_2$ for two hours. Bubbling pure oxygen for a comparable period was also successful. Air oxidation required several days and lead to somewhat erratic results due to the oxidation of the dimethylglyoxime over this period of time. After $PbO_2$ or $O_2$ treatment the solution was placed in the polarographic cell, oxygen removed by passing nitrogen for 10 min (a longer period allows some decomposition), and the polarogram recorded. A typical polarogram is shown in Fig. 1. The concentration range studied could not be extended above $1 \cdot 10^{-3} M$ due to erratic behavior on the diffusion plateau. This is apparently due to the limited solubility of nickel(II) dimethylglyoxime in 1.5 $M$ NaOH, the erratic behavior resulting from precipitation at or near the electrode surface.

Extensive analytical polarographic data was not gathered since spectrophotometric methods[2] would probably be superior in this concentration range. However, much information was gained from the polarographic study. The diffusion current constant, $I$, was found to have a value of $2.4 \pm 0.1$. This value of $I$ is in agreement with that of 2.4 for lead tartrate complex (a presumably similar ion) in sodium hydroxide and thus indicates a 2 electron reduction. That the reduction current was diffusion controlled was shown by the fact that $i/\sqrt{h}$ was constant to 2%. The half wave potential was found to be $-0.297$ V *vs.* S.C.E. and was independent of the nickel and dimethylglyoxime concentrations over at least a ten fold range. Thus the reduction is probably reversible and the same number of dimethylglyoxime ligands are associated with the oxidized (red) form and the nickel(II) complex. A plot of log $i/(i_d - i)$ *vs.* $E$ yielded a straight line with a slope of 0.030, confirming a reversible 2 electron reduction.

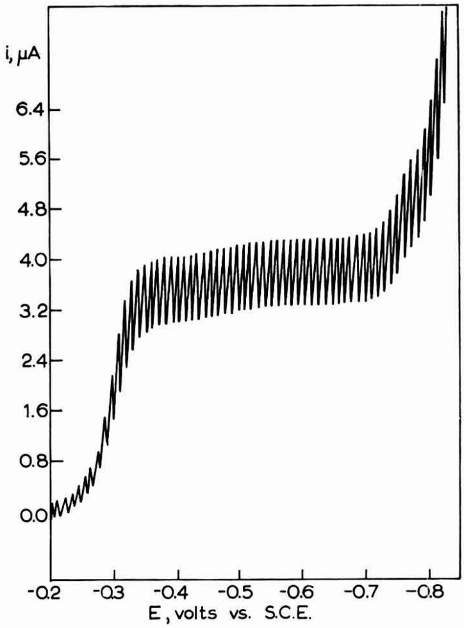

Fig. 1. Polarogram of $0.5 \cdot 10^{-3} M$ nickel in a solution 1.5 $M$ in NaOH and 0.1 $M$ in dimethylglyoxime. Oxidized with $PbO_2$, the excess of which was removed by filtration just before the polarogram was taken.

On the basis of the above data the electrode reaction would appear to be

$$\mathrm{Ni(IV)D_x} + 2\,e \rightleftharpoons \mathrm{Ni(II)D_x}$$

where x is 3 or more. Actually no statement can be made as to whether or not hydroxide ion participates in the electrode reaction. Variations of hydroxide concentration were not attempted since a large enough change to result in detectable half-wave potential shifts could not be accomplished without making the red complex unstable.

*Controlled potential electrolysis* Although the polarographic data strongly indicates a two electron reduction, further tests were desired to confirm the fact that a two electron reduction was indeed occurring and that the reduction was between Ni(IV) and Ni(II), and did not involve the reduction of molecular oxygen bound to the nickel as suggested in ref. 7.

A controlled potential electrolysis, with a mercury pool electrode, was run at −0.60 V *vs.* S.C.E. This potential is reducing enough to reduce the red complex (see Fig. 1) but not so reducing that nickel(II) dimethylglyoxime or hydrogen peroxide (which might result from the reduction of bound molecular oxygen) would react. The solutions contained $0.25 \cdot 10^{-3}\,M$ of nickel(II) and $10 \cdot 10^{-3}\,M$ of dimethylglyoxime in 100 ml of 1.5 *M* NaOH. Complete oxidation was accomplished by treatment with $PbO_2$ for five hours. The excess solid $PbO_2$ was removed by filtration just before the electrolysis. Dissolved oxygen was removed by a stream of nitrogen.

The average *n* value for the controlled potential reductions at the mercury cathode was 1.9. This value fell slightly short of 2.0 due to electrode fouling by nickel(II) dimethylglyoxime precipitating near the end of the electrolysis and possibly to a decomposition of the red nickel(IV) dimethylglyoxime complex. The solution resulting from the electrolysis was light yellow and had the same spectra as the nickel(II) dimethylglyoxime solution made by mixing the air-free components. A "titanium spot test" for hydrogen peroxide was negative.

By recording current-reversal chronopotentiograms using a platinum working electrode it was found that air-free nickel(II) dimethylglyoxime could be oxidized at $E_{\frac{1}{4}} = +0.22$ V *vs.* S.C.E. and a reverse (reduction) wave (having a transition time one-third that of the oxidation transition time) with an $E_{\frac{1}{4}} = -0.34$ V *vs.* S.C.E. could be recorded. The opposite case could also be accomplished, starting with nickel(IV)-dimethylglyoxime. When the current was varied, the quantity $i\tau^{\frac{1}{2}}$ was found to be constant. It may thus be concluded that the electrode reaction at platinum is diffusion controlled and of the simple irreversible type[10].

On the basis of the above values of $E_{\frac{1}{4}}$, a controlled potential electrolysis study was initiated at a platinum electrode. An air-free solution containing $0.0500 \cdot 10^{-3}\,M$ of nickel(II) and $0.3 \cdot 10^{-3}\,M$ of dimethylglyoxime in 1.5 *M* sodium hydroxide was made up under nitrogen in the controlled potential electrolysis cell. The passage of nitrogen was continued throughout the experiment. The solution was oxidized electrolytically at a controlled potential of +0.40 V *vs.* S.C.E. The deep red color of the oxidized nickel dimethylglyoxime complex rapidly appeared, indicating oxygen or oxygen producing species to be unnecessary. The electrolysis current eventually dropped to a low but finite value (direct oxidation of dimethylglyoxime). After correction for this background current an *n* value of 1.92 was calculated. The working electrode was now made the cathode, the controlled reduction potential being −0.40 V *vs.* S.C.E. As the electrolysis proceeded the red color faded to the original yellow. The *n* value for reduction was found to be 1.99. No background correction was necessary.

Since the oxidation and subsequent reduction of nickel in a solution of dimethylglyoxime–1.5 *M* sodium hydroxide showed analytical promise for a range of nickel concentrations generally too high for spectrophotometric work, an accuracy and interference study was made. The electrolyte, the concentrations of which were 1.5 *M* in sodium hydroxide and 0.01 *M* in dimethylglyoxime, was placed in the cell. A nickel sample was added, some of which was oxidized by dissolved air. The oxidation was completed by controlled potential electrolysis at +0.30 V *vs.* S.C.E. The quantity of electricity passed was not recorded. When the current dropped to a low constant value, the electrolysis was stopped and oxygen removed by bubbling nitrogen through the solution. The oxidized nickel was then reduced at −0.40 V *vs.* S.C.E. and the coulombs used to accomplish this, recorded. Table I indicates the results obtained and the effect of interferences. In general, results can be obtained with an accuracy of better than 0.5%. Manganese and iron appear to interfere, the latter apparently due to electrode fouling which causes incomplete oxidation of the nickel.

TABLE 1

THE CONTROLLED POTENTIAL DETERMINATION OF NICKEL

| *Nickel taken (mequiv.)* | *Nickel found (mequiv.)* | *Added ion (mequiv.)* |
|---|---|---|
| 0.0989 | 0.0983 | |
| | 0.0986 | |
| 0.0500 | 0.0505 | |
| | 0.0500 | |
| | 0.0499 | |
| | 0.0499 | $Co^{2+}$ (0.05) |
| | 0.0622 | $Mn^{2+}$ (0.02) |
| | 0.0483 | $Fe^{3+}$ (0.02) |
| 0.0300 | 0.0288 | $Fe^{3+}$ (0.02) |
| | 0.0296 | $Co^{2+}$ (0.05) |
| | 0.0301 | $Al^{3+}$ (0.03) |
| | 0.0303 | $Zn^{2+}$ (0.05) |
| | 0.0302 | $Cl^{-}$ (0.09) |

The controlled-potential electrolysis evidence seems to substantiate the idea that the red-colored material is, indeed, a nickel(IV) dimethylglyoxime complex, rather than one of nickel(III) or involving an oxygen carrying chelate of nickel(II). Some additional evidence was found through spectrophotometry and magnetic measurements.

*Spectrophotometry* One of the main points in favor of the idea that the red colored complex was of the oxygen carrying chelate variety was that the color could be changed to light yellow by heating to about 70° or holding the solution under partial vacuum for a few minutes[7]. At first thought, it would seem that these procedures remove oxygen from solution and thus reverse a reversible oxygen chelate formation. Indeed, if nitrogen is passed through a previously oxidized nickel dimethylglyoxime solution, the color also fades slowly (and the polarographic wave of Fig. 1 disappears). In view of the controlled potential electrolysis experiments and the fact that dimethylglyoxime is oxidizable at a platinum electrode at potentials slightly more oxidizing than necessary for the formation of nickel(IV), it appears that the nickel(IV) dimethylglyoxime complex is unstable. The nickel(IV) is a strong enough oxidizing agent to oxidize dimethylglyoxime slowly, probably to furoxane[6]. This would also explain the disappearance of the red color on heating, etc.

To investigate this reaction more carefully a sample of nickel(IV) in excess oxygen-free dimethylglyoxime solution, 1.5 $M$ in sodium hydroxide, was sealed in a spectrophotometer cell and spectra taken over a period of several days (Fig. 2). The final spectra is identical with that of unoxidized nickel(II) dimethylglyoxime. The fact that the complex changes spontaneously to the yellow nickel(II) complex in a sealed vessel at room temperature indicates that the instability is only accelerated by heat rather than being caused by it. The application of vacuum simply removes dissolved oxygen which otherwise would continue to oxidize the nickel. This evidence again supports the idea that the red complex may well be a nickel(IV) species—the nickel(IV) being a strong enough oxidizing agent to react with dimethylglyoxime.

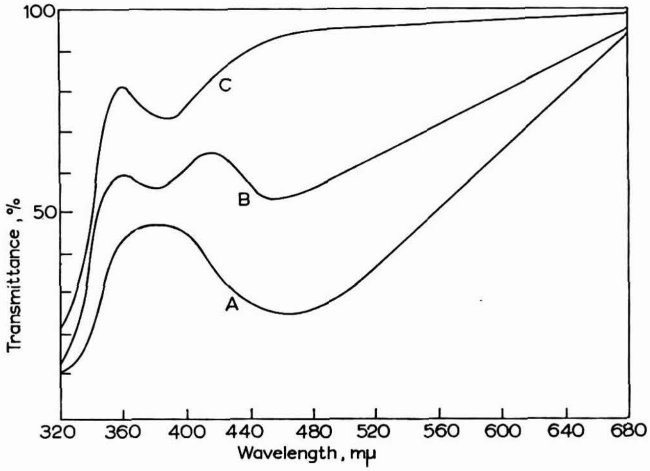

Fig. 2. Absorption spectra of 8.0 · $10^{-5}$ $M$ nickel in a solution 1.5 $M$ in NaOH and 4 · $10^{-4}$ $M$ in dimethylglyoxime. The solution was treated with oxygen, the excess oxygen removed with nitrogen and sealed in the absorption cell. Curve A, taken immediately; curve B, after 24 h; curve C, after 85 h (no further change observed.)

OKÁČ AND ŠIRNEK[5] have shown by means of photometric titrations that the red complex has a ratio of three dimethylglyoxime ions for each nickel ion, and by means of paper electrophoresis that the charge on the red complex is −2. Experiments in this laboratory tend to confirm these results. In the light of this work and the polarographic studies, the electrode reaction at mercury and probably platinum electrodes can be written

$$NiD_3^{4-} \rightleftharpoons NiD_3^{2-} + 2e$$

The nickel(IV) complex can then decompose slowly at room temperature

$$D^{2-} + NiD_3^{2-} = NiD_3^{4-} + D^{ox}$$

where $D^{ox}$ is most likely furoxane. (An attempt to isolate furoxane was unsuccessful but it is a known oxidation product of dimethylglyoxime[11]).

*Magnetic data* In an effort to establish definitely that the oxidation state of nickel in the red complex was indeed +4, a magnetic susceptibility study was conducted.

The results of these determinations yielded for the complex effective molar susceptibilities, $X_M^{\text{eff}}$, of $+640 \cdot 10^{-6}$ and $+648 \cdot 10^{-6}$ for nitrogen and oxygen saturated solutions respectively. (Solutions saturated in oxygen were corrected for the susceptibility of the dissolved oxygen.) The magnetic moment calculated from these data is 1.23 ± 0.02 B.M., assuming a simple Curie Law behavior. The temperature variation studies showed a change in susceptibility of 2.4 ± 1.0% within the range 299°–339°K, whereas the expected temperature change (assuming the Curie temperature relationship) for a paramagnetic ion with one unpaired electron should have been at least 4% within the limits of experimental error. Thus the observed temperature variation is just within the limits of experimental error, while that expected for one unpaired electron is a factor of three times greater than what could be attributed to experimental error. Hence we are forced to conclude on the basis of these limited studies that the susceptibility of $\text{Ni(IV)D}_3^{-2}$ is independent of temperature, at least within the restricted temperature range of investigation and high dilution conditions. Although the value determined for the magnetic moment at ambient temperature should be reasonably accurate, too much significance should not be attached, however, to the temperature variation studies. If the susceptibility is indeed temperature independent than the susceptibility must be of the high frequency type, wherein the paramagnetism arises from mixing of a singlet ground state with low lying singlet excited states *via* orbital angular moments. However, the observed magnetic moment is too large by about a factor of two to account for this effect alone.

Magnetic moments of the magnitude found here have also been reported for other Ni(IV) compounds[12] as well as for Ni(II) complexes in planar four-coordination with a diamagnetic ground state[13]. In the latter cases, if the Ni(II) ion is in a weak tetragonal field then the paramagnetism should arise from mixing of the singlet ground state with a thermally accessible triplet state of the complex[14]. Although alternative mechanisms may be equally valid for explaining the anomalous magnetic behavior of four-coordinated Ni(II) complexes[13], the thermal population of a triplet level is the most reasonable explanation for the anomalous magnetic behavior of a six-coordinated Ni(IV) complex.

That dimethylglyoxime is a strong field ligand is evidenced by the fact that $\text{Ni(II)D}_2$, an effectively square planar complex, is diamagnetic. Since the effective ligand field strength increases proportionally with increasing positive charge on the central metal atom, then octahedrally coordinated $\text{Ni(IV)D}_3^{2-}$ should certainly exist in a diamagnetic singlet ground state. Consequently, in addition to high frequency effects, the paramagnetism observed in this latter complex should result from the population of a thermally accessable triplet level. If this interpretation is correct then the magnetic moment should increase with temperature, which has not yet been completely confirmed for the complex in solution.

Future investigations will include the attempt to isolate the complex and subject it to critical magnetic and spectral investigations. Theoretical correlation with the experimental observables will also be attempted in an effort to gain a better understanding of the bonding in this complex.

## ACKNOWLEDGEMENTS

This investigation was supported in part by Public Health Service Grant AMO8248 from the National Institute of Arthritis and Metabolic Diseases.

## SUMMARY

The red solutions of nickel dimethylglyoxime in strongly basic solution have been studied by electrochemical, spectrophotometric and magnetic methods. It is concluded that the red complex is a species of Ni(IV). A controlled potential coulometric method for the analysis of nickel is also presented.

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# DROP-TIME DEPENDENCE OF A.C. POLAROGRAPHIC PEAK HEIGHTS

G. H. AYLWARD AND J. W. HAYES*

*School of Chemistry, University of New South Wales, Kensington, N.S.W. (Australia)*

(Received August 3rd, 1964)

## INTRODUCTION

FLORENCE AND AYLWARD[1] reported the dependence of the a.c. polarographic peak height on the drop-time for the reduction of Eriochrome Violet B (5-sulpho-2-hydroxybenzeneazo-2'-naphthol) and indicated that a number of other organic and inorganic depolarizers behave similarly. A number of other authors[2-6] have reported subsequent theoretical and experimental studies concerned with the drop-time dependence of a.c. polarographic currents. When some kinetic process, as well as diffusion, contributes to the steady mass transfer of depolarizer, the electrode surface concentrations of oxidant and reductant are time-dependent and, hence, the faradaic alternating current varies with drop-time.

In this paper we present detailed experimental results which show the drop-time dependence of peak heights for systems involving quasi-reversible electron transfer, coupled chemical reactions, rate limited surface coverage, and amalgam formation.

## QUASI-REVERSIBLE ELECTRON TRANSFER REACTION

By applying a steady-state assumption, we have extended BAUER's equation[7] for the amplitude of the faradaic alternating current to cover quasi-reversible systems[3]. This expression (eqn. 1) predicts that when the electron-transfer reaction is quasi-reversible in the d.c. sense, the amplitude of the alternating current will be dependent upon the drop-time. When the electron-transfer is reversible in the d.c. sense, this current is independent of drop-time.

$$\Delta i = \frac{-n^2 F^2 A\, \Delta v\, C^\circ{}_O k_s \left\{\alpha + k_s\left(\frac{3\pi t'}{7D_R}\right)^{\frac{1}{2}} \exp(\beta P)\right\} \exp(-\alpha P)}{RT\left\{1 + k_s\left(\frac{3\pi t'}{7D_O}\right)^{\frac{1}{2}} \exp(-\alpha P) + k_s\left(\frac{3\pi t'}{7D_R}\right)^{\frac{1}{2}} \exp(\beta P)\right\}(1 + 2z + 2z^2)^{\frac{1}{2}}} \qquad (1)$$

A numerical analysis shows that this expression is in good agreement with the more rigorous equation of MATSUDA[8].

In Table 1** the values of the alternating current at different drop-times for the

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* Present address: Department of Chemistry, University of North Carolina, Chapel Hill, N.C., U.S.A.

** All polarograms in this paper were taken using an alternating voltage of 15 mV r.m.s. and a frequency of 60 c per sec. Peak heights are quoted without subtraction of base current.

TABLE 1

REVERSIBLE AND QUASI-REVERSIBLE REDUCTIONS

| *Drop-time (sec)* | *Peak heights ($\mu A$ r.m.s.)* | | |
|---|---|---|---|
| | [a]$[Fe(C_2O_4)_3]^{3-}$ | [b]$UO_2^{2+} \rightarrow UO_2^{+}$ | [c]*Cd–EDTA* |
| 2.8 | 18.8 | 32.0 | 11.0 |
| 4.0 | 18.8 | 32.0 | 10.0 |
| 6.7 | 18.9 | 32.0 | 6.8 |
| 10.0 | 19.0 | 32.0 | 5.8 |

[a] Concn. of $[Fe(C_2O_4)_3]^{3-}$ : $1.0 \times 10^{-3}$ *M*. Supporting electrolyte : 0.1 *M* $Na_2C_2O_4$; 0.9 *M* $NaClO_4$.
[b] Concn. of $UO_2^{2+}$ : $2.0 \times 10^{-3}$ *M*. Supporting electrolyte : 1 *M* $NaClO_4$, pH 3.
[c] Concn. of cadmium–EDTA complex: $4 \times 10^{-3}$ *M*. Supporting electrolyte: $5 \times 10^{-3}$ *M* EDTA, 0.1 *M* $CaCl_2$; 0.2 *M* acetate buffer, pH 3.0.

quasi-reversible reduction of the ethylenediaminetetraacetatocadmate(II) (cadmium–EDTA) are compared to those given by two reversible systems. The peak height for the reduction of the cadmium–EDTA complex decreases as the drop-time is increased, whilst the peak heights for the reversible reductions are independent of the drop-time, within experimental error. The slight drop-time dependence observed in the case of the trisoxalatoferrate(III) system is due to the damping effect of the meter used to measure the alternating current.

### COUPLED CHEMICAL REACTIONS

When the frequency of the superimposed alternating potential is low and the rate constant for the electron transfer is high, the relationship between the amplitude of the faradaic alternating current and the surface concentrations of oxidant and reductant can be expressed by eqn. (2)

$$\Delta i = \frac{-n^2 F^2 A\, \Delta v (\omega D)^{\frac{1}{2}}}{RT} \cdot \frac{C_O C_R}{C_O + C_R} \tag{2}$$

$\Delta i$ will have its maximum value when $(C_O C_R)/(C_O + C_R)$ is a maximum, *i.e.*, when $C_O = C_R$. This equation can be applied to determine the peak magnitude of the alternating current for a system in which a chemical reaction is coupled with the fast electron-transfer reaction, provided that the periodic mass transfer remains diffusion-controlled. Clearly, when the chemical reaction affects the steady concentrations of oxidant and reductant at the electrode surface, the alternating current will exhibit a drop-time dependence.

### (*a*) *Following reaction*

Equation (3) shows dependence of the peak height ($\Delta i_{E_s}$) on the drop-time, and the rate of the following reaction[3].

$$\Delta i_{E_S} = \frac{-n^2 F^2 A\, \Delta v\, C°_O (\omega D_R)^{\frac{1}{2}}}{RT \left\{ \left( \frac{D_R}{D_O} \right)^{\frac{1}{2}} + \left( \frac{3\pi k_f D_R t'}{7 D_O} \right)^{\frac{1}{2}} \right\}^2} \tag{3}$$

This equation applies provided that the electron-transfer reaction is reversible and the value of $k_f$ is less than $\omega$ but greater than about 10 sec$^{-1}$ [9]. The peak height decreases with increasing drop-time. Under these conditions the expression for the phase angle is the same as that obtained when the mass transfer is a diffusion process.

The mechanism of the oxidation of *p*-amino phenol has been shown to involve the hydrolysis of the intermediate *p*-quinoneimine[10-12]. In acetate buffer, the a.c. polarographic wave that corresponds to the reversible d.c. step of *p*-amino phenol decreases in height as the drop-time is increased (Table 2).

TABLE 2

OXIDATION OF *p*-AMINO PHENOL

Concentration of *p*-amino phenol : $1 \times 10^{-3}$ *M*. Supporting electrolyte: 0.2 *M* acetate buffer, pH 5; 0.9 *M* $NaClO_4$.

| *Drop-time (sec)* | *Peak height (µA r.m.s.)* |
|---|---|
| 2.8 | 84 |
| 4.0 | 83 |
| 6.0 | 81 |
| 9.8 | 74 |

Two other electrode processes involving following chemical reactions have been studied in considerable detail, *viz.*, oxidation of cadmium amalgam in a solution containing EDTA, and the reduction of the ethylenediaminetetraacetatoeuropate(III) complex to the europium(II) complex in the presence of calcium ions. These results will be reported in later papers.

### (*b*) *Preceding reactions*

When a chemical reaction precedes the electron-transfer reaction, the concentration of depolarizer at the electrode surface increases with time. The quasi-steady-state approach may be used to determine these concentrations[13]. Consequently, the peak height of the a.c. polarogram will increase, within certain limits, with increasing drop-time.

TABLE 3

REDUCTION OF CADMIUM IONS FORMED BY DISSOCIATION OF THE ETHYLENEDIAMINETETRA-ACETATOCADMATE(II) COMPLEX

Concentration of cadmium–EDTA complex: $4 \times 10^{-3}$ *M*. Supporting electrolyte: $5 \times 10^{-3}$ *M* EDTA; 0.1 *M* $CaCl_2$; 0.2 *M* acetate buffer, pH 3.0.

| *Drop-time (sec)* | *Peak height (µA r.m.s.)* |
|---|---|
| 2.8 | 3.6 |
| 4.0 | 3.8 |
| 6.0 | 4.1 |
| 9.8 | 4.3 |

The height of the first step in the reduction of the cadmium–EDTA complex in the absence of an excess of free EDTA depends upon the rate of dissociation of the complex[13]. The a.c. wave height for this reduction increases with increase in drop-time (Table 3).

### (c) *Regeneration reactions*

In cases where the depolarizer is regenerated by a chemical reaction *e.g.*, disproportionation, the steady electrode-surface concentrations of oxidant and reductant are time-dependent. This is illustrated by the decrease in the a.c. wave height with increase in drop-time for the reduction of uranyl(VI) to uranyl(V) ions in perchloric acid solution (Table 4). Under these conditions disproportionation of the uranyl(V) ions to tetravalent and hexavalent uranium takes place[14].

TABLE 4

REDUCTION OF URANYL(VI) TO URANYL(V)

Concentration of $UO_2(ClO_4)_2$ : 2 × $10^{-3}$ *M*. Supporting electrolyte: 1 *M* $NaClO_4$; $HClO_4$.

| *Drop-time (sec)* | *Peak height (μA r.m.s.)* | |
|---|---|---|
| | *0.5 M $HClO_4$* | *1.0 M $HClO_4$* |
| 2.8 | 31.2 | 30.8 |
| 4.0 | 31.2 | 30.8 |
| 6.6 | 30.9 | 30.4 |
| 9.8 | 30.8 | 29.9 |

## ADSORPTION PROCESSES

Since the rate of adsorption can be limited by mass transfer of the adsorbable substance, or by the rate at which adsorption equilibrium is attained[15], the concentration of an adsorbate at a dropping mercury electrode may be time-dependent. It is expected that this effect would be noticeable as a drop-time dependence of the peak height in a.c. polarography and tensammetry.

### (a) *Adsorption of non-electroactive species*

The effect of slow adsorption of a non-electro-active species upon the d.c. polarographic current is well known[15,16,17]. The effect of the addition of Triton X-100 on

TABLE 5

REDUCTION OF ETHYLENEDIAMINETETRAACETATOCUPRATE(II) IN THE PRESENCE OF TRITON X-100

Concentration of Cu $Y^{2-}$ : 1 × $10^{-3}$ *M*. Supporting electrolyte : 1 × $10^{-2}$ *M* EDTA; 0.1 *M* acetate buffer, pH 4.3.

| *Drop-time (sec)* | *Peak height (μA r.m.s.)* | | |
|---|---|---|---|
| | *Concn. Triton X-100* | | |
| | *0%* | *1.5 × $10^{-3}$%* | *3.0 × $10^{-3}$%* |
| 3.1 | 15.8 | 6.0 | 2.0 |
| 4.7 | 15.8 | 3.6 | 1.8 |
| 9.8 | 16.1 | 2.3 | 1.3 |

the a.c. polarographic peak height for the reduction of the ethylenediaminetetraacetatocuprate(II) complex is shown in Table 5. Similar results were observed when Triton X-100 was added to other depolarizer solutions. As the drop-time is increased, the more complete is the coverage of the electrode surface by non-electroactive species. This causes greater inhibition of the electron-transfer process and hence a lowering of the peak height.

### (b) *Tensammetric waves*

The heights of tensammetric waves of cyclohexanol, *sec.*-octanol, pyridine, *n*-butanol, *n*-propanol, phenol, catechol, pyrogallol, and resorcinol were found to be independent of drop-time in 1 *M* sodium sulphate. This apparently indicates a rapid attainment of adsorption equilibrium according to the criterion of DELAHAY AND TRACHTENBERG[15].

The height of the positive tensammetric wave for camphor was found to decrease with increasing drop-time (Table 6). This is in agreement with the mechanism of slow adsorption[16].

BIEGLER[18] has shown that the heights of the tensammetric waves obtained for bromide and chloride ions increase with increasing drop-time. He explains this in terms of diffusion-control of the adsorption process.

TABLE 6

TENSAMMETRY OF CAMPHOR

$5 \times 10^{-2}$ *M* camphor in 0.1 *M* potassium nitrate

| *Drop-time (sec)* | *Peak height (μA r.m.s.)* |
|---|---|
| 3.0 | 25.2 |
| 4.6 | 25.1 |
| 6.0 | 25.0 |
| 8.4 | 23.0 |

## AMALGAM FORMATION

When metal ions are reduced to an amalgam-forming metal a slight increase in peak height with increasing drop-time is observed. In the oxidation of an amalgam, a decrease in peak height with increasing drop-time is found. Table 7 shows some results obtained for systems of this type.

TABLE 7

REDUCTION OF METAL IONS TO AMALGAMS AND OXIDATION OF CADMIUM AMALGAM

Supporting electrolyte: 0.1 *M* $HClO_4$

| *Drop-time (sec)* | *Peak heights (μA r.m.s.)* | | | | |
|---|---|---|---|---|---|
| | $Cd^{2+}$ $2 \times 10^{-3}$ *M* | $Cu^{2+}$ $2 \times 10^{-3}$ *M* | $Pb^{2+}$ $2 \times 10^{-3}$ *M* | $Tl^{+}$ $1 \times 10^{-3}$ *M* | *Cd(Hg)* $2 \times 10^{-4}$ *M* |
| 3.0 | 69 | 65 | 69 | 37 | 29.8 |
| 4.4 | 72 | 68 | 72 | 38 | 29.0 |
| 5.8 | 74 | 70 | 76 | 41 | 27.6 |

STREHLOW AND VON STACKELBERG[19] have shown that in the reduction of amalgam-forming metal ions the tangential streaming within the drop causes an enhanced removal of metal from the electrode surface, particularly during the early stages of drop-life. Towards the end of drop-life, diffusion becomes the chief mass transfer process. As the drop time is increased, the fraction of drop-life over which streaming occurs is decreased. Consequently, the concentration of metal at the electrode surface at the end of drop-life increases with drop-time. This causes an increase in the peak height of the a.c. polarogram with increasing drop-time.

In amalgam-polarography streaming increases the rate of transfer of the depolarizer to the electrode surface. As the drop-time is increased, the fraction of drop-life over which streaming takes place is decreased, and so the rate of arrival of depolarizer at the electrode surface is decreased. This gives a decrease in peak height with increasing drop-time. The "wedge effect" enhances these concentration changes at the electrode surface[19].

Concentration changes such as these would be expected to give rise also to a shift in the half-step potential with drop-time. Such a shift has been observed by STREHLOW AND VON STACKELBERG[19] who explained their results in a manner similar to that given.

TANAKA *et al.*[20] have examined the peak-height, drop-time relationship for a rapidly-dropping mercury electrode (RADME) for the reduction of cadmium ions in 1 *M* potassium nitrate solution. Although the "rinse effect"[19] is particularly evident on the d.c. polarograms under these conditions, the heights of the a.c. polarograms change only slightly with drop-time. This is possibly because at such short drop times (0.6–1.9 sec) streaming takes place over the whole of the drop-life, and the increase in electrode-surface concentration (which would take place at longer drop times) does not occur.

## CONCLUSION

It has been stated[21,22] that the drop-time independence of the peak current in a.c. polarography is of advantage in analytical work. Since there has been little published experimental work designed to test this independence, it appears that this statement has been made mainly on the basis of theoretical equations derived for fast electron transfer processes.

Whenever the concentration of depolarizer at the electrode surface is a function of time, the period of which is of the same order as the drop-time, the peak height will be drop-time dependent. In cases where the period of the time-dependent concentration change is of the order of the frequency of the alternating voltage, changes in the amplitude and phase angle of the concentration wave will occur[23–25] and the drop-time dependence will be less important.

## NOTATION

| | |
|---|---|
| $A$ | electrode surface area; |
| $C_{O,R}$ | surface concentrations of oxidant and reductant; |
| $C^{\circ}{}_O$ | concentration of oxidant in the bulk of the solution; |
| $D_{O,R}$ | diffusion coefficient of $O,R$; |
| $E$ | direct potential; |
| $E^{\circ}$ | formal potential; |
| $E_s$ | summit potential; |

| | |
|---|---|
| $F$ | Faraday number; |
| $\Delta i$ | amplitude of polarographic alternating current; |
| $k_f$ | rate constant of first order following chemical reaction; |
| $k_s$ | formal heterogeneous rate constant of electron-transfer reaction; |
| $n$ | number of electrons involved in electrode reaction; |
| $P$ | $=(nF/RT)\ (E - E^\circ)$; |
| $R$ | molar gas constant; |
| $T$ | absolute temperature; |
| $t'$ | drop time; |
| $\Delta v$ | amplitude of applied alternating voltage; |
| $z$ | $=k_s/(2\omega D_R)^{\frac{1}{2}}\{(D_R/D_O)^{\frac{1}{2}} + \exp P\} \exp(-\alpha P)$; |
| $\alpha$ | cathodic transfer coefficient; |
| $\beta$ | $1 - \alpha$ (anodic transfer coefficient); |
| $\omega$ | angular frequency. |

## SUMMARY

Experimental evidence of the drop-time dependence of the peak height in a.c. polarography is presented for a quasi-reversible electron-transfer process and a number of reductions and oxidations involving coupled chemical reactions, rate limited surface coverage, and amalgam formation. Each process is discussed in relation to the kinetics of the overall electrode reaction. In the systems reported, drop-time dependence is exhibited whenever a form of mass transfer other than, or as well as, diffusion operates.

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# ISOTHERMS FOR HYDROGEN ADSORPTION ON PLATINUM ELECTRODES IN SULFURIC ACID SOLUTION

M. W. BREITER

*General Electric Research Laboratory, Schenectady, N. Y. (U.S.A.)*

(Received August 6th, 1964)

## INTRODUCTION

The equilibrium properties of adsorbed hydrogen atoms can be easily studied[1,2] by electrochemical methods on platinum metals (Pt, Ir, Rh, Pd) since the exchange current density $I_0$ ($U$) of the Volmer reaction

$$H^+ + e = H_{ad} \tag{1}$$

at a potential $U$ in the region of hydrogen adsorption is relatively large. The equilibrium of eqn. (1) is practically established for charging curves or voltammetric current–potential curves if the maximum value of the current density $I$ is much smaller than $I_0$ ($U$). The contributions of the Heyrovský reaction

$$H^+ + H_{ad} + e = H_2 \tag{2}$$

and of the Tafel reaction

$$H_{ad} + H_{ad} = H_2 \tag{3}$$

are negligible[1] when working at anodic potentials $U > 0.06$ V. Here the potential $U$ refers to a hydrogen electrode in the same electrolyte and at the same temperature as the test electrode.

The nearly linear dependence of hydrogen coverage upon the potential which was found to hold in a large potential range by anodic charging curves led to the interpretation[1,3] that the specific heterogeneity of the platinum surface can be described satisfactorily by a linear decrease of the heat of adsorption with the hydrogen coverage (range of medium coverage of the Temkin isotherm[4]). However, measurements of the pseudo-capacity of adsorbed hydrogen at small frequencies revealed a more detailed structure of the surface with two distinct regions for hydrogen adsorption[5,6]. Hydrogen adsorption at room temperature obeyed[5] approximately a simple Langmuir isotherm in each of these regions. Potentiostatic current–potential curves which were measured by cyclic voltammetry[7,8] or by single anodic sweeps[9] confirmed the existence of these regions.

Since the heat of hydrogen adsorption decreases[8,10] with coverage on platinum electrodes in aqueous solutions, it was suggested that the Langmuir isotherm holds approximately for each of the regions because of a compensatory effect[11]. The decrease of the heat of adsorption is nearly compensated by the change of the entropy term $T\Delta s$ so that the standard free energy change $\Delta g_0$ is nearly independent of coverage. The existence of two types of hydrogen adsorption on platinum is well-known[12-16] from studies in the gas phase.

The purpose of this report is to test the applicability of the Langmuir isotherm and of the Frumkin isotherm[17] to hydrogen adsorption in each of the different regions for smooth platinum electrodes in 1 $N$ $H_2SO_4$ between 0° and 70°. Cyclic voltammetry was used as in previous communications[7,8]. A periodic voltage of triangular shape was applied between 0.05 V and 1.5 V at 30 mV/sec, and the $I-U$ curves were recorded. The intermediate formation and reduction of the oxygen layer leads to a reproducible surface state.

## THEORETICAL

The properties of the platinum surface are revealed better by the $I-U$ curves than by the adsorption isotherms which are obtained by their integration. Therefore, the fit between experimental and calculated current densities at a given potential was studied. If the surface consists of $n$ distinct regions with a partial coverage $\theta_i \leqslant 1$ and a charge equivalent of $\Gamma_i F$ for the mono-layer formation of hydrogen atoms, the current density during the anodic removal of the hydrogen layer as a function of time $t$ is:

$$I = -\sum_{i=1}^{n} \Gamma_i F \frac{d\theta_i}{dt} \tag{4}$$

The removal occurs under equilibrium conditions:

$$U = \frac{-RT}{2F} \ln \frac{p_{H_2}}{{}_0p_{H_2} - p_{el}} \tag{5}$$

$$\theta_i = f_i(p_{H_2}) = h_i(U) \tag{6}$$

Here $p_{H_2}$ designates the hydrogen pressure at the surface, ${}_0p_{H_2}$, is equal to the barometric air pressure, and $p_{el}$ is the vapor pressure of the electrolyte at the temperature $T$. The functions $f_i(p_{H_2})$ and $h_i(U)$ are determined by the adsorption isotherm. It follows that

$$I = -\sum_{i=1}^{n} \Gamma_i F \frac{dh_i}{dU}\frac{dU}{dt} = -\sum_{i=1} v\Gamma_i F \frac{dh_i}{dU} \tag{7}$$

Here $v$ is the velocity of the voltage sweep.

Assuming a Langmuirian type of adsorption

$$RT \ln p_{H_2} = \Delta g_{0,i} + 2RT \ln \frac{\theta_i}{1 - \theta_i} \tag{8}$$

the standard free energy of adsorption $\Delta g_{0,i}$ of the region $i$ can be computed for $\theta = 1/2$ from the potential of the peak current of the $I-U$ curve in the respective region, since each of the single oxidation waves is practically symmetrical with respect to their peak. $\Gamma_i F$ can be expressed by the peak current $I_i$ so that eqn. (7) reads:

$$I = 4 \cdot \sum_{i=1}^{n} I_i \theta_i (1 - \theta_i) \tag{9}$$

The current density $I$ was computed from eqn. (9) as a function of $U$ and $T$ after determining the values of the parameters $\Delta g_{0,i}$ and $I_i$ for each region from the experimental $I-U$ curves at a given temperature.

A similar approach was taken under the assumption of Frumkin's isotherm:

$$RT \ln p_{H_2} = \Delta g_{0,i} - 4RT\beta_i\theta_i + 2RT \ln \frac{\theta_i}{1 - \theta_i}. \qquad (10)$$

This treatment involves one more parameter $\beta_i$ for each region than for the preceding one. The parameter $\beta_i$ describes the interaction between the adsorbed particles ($\beta > 0$; attraction, $\beta < 0$: repulsion, $\beta = 0$: Langmuirian adsorption). Equation (7) reads:

$$I = \sum_{i=1}^{n} I_i(4 - 2\beta_i) \frac{\theta_i(1 - \theta_i)}{1 - 2\beta_i\theta_i(1 - \theta_i)}. \qquad (11)$$

The computations were made with the aid of suitable programs by the GE 225 computer. In the case of the Frumkin isotherm, the transcendental eqn. (10) was solved approximately to three decimals for $\theta$ at a given $p_{H_2}$ (or $U$) in order to compare the computed and measured current density at a given potential.

## EXPERIMENTAL

The measurements were made in a Pyrex glass vessel of conventional design. The test electrode was a bright platinum wire of purity 99.99% and a geometric area of 0.5 $cm^2$. The electrolyte was stirred with purified helium before each run. The stirring was then stopped, and the data were taken in quiescent solution. The hydrogen reference electrode was in a compartment separated by a porous disk from the compartment of the test electrode. The temperature was maintained at $\pm$ 0.5°. The $I-U$ curves were recorded with the Varian X-Y F80 recorder which allowed large resolution.

Traces of impurities were successfully removed from the electrolyte by the following procedure. Hydrogen and oxygen were evolved simultaneously at 1 amp for an hour at 70° in the test vessel under helium stirring. The anode was a large platinum cylinder; a platinum wire served as the cathode. Hydrogen peroxide was formed to some extent, and the electrolyte was stirred with purified hydrogen for an hour at 70° in the presence of the platinum cylinder in order to decompose the hydrogen peroxide. $I-U$ curves at 70° did not exhibit waves due to hydrogen peroxide or other impurities after this pre-treatment, although the existence[18] of small anodic waves in the untreated solution at $T \geqslant 50°$ had indicated the presence of impurities.

## LANGMUIR ISOTHERM

The results of the computation are compared with the experimental data in Fig. 1(a) for 0° and in Fig. 1(b) for 70°. The experimental data end at 0.06 V but the calculation was extended into the region of hydrogen evolution ($U < 0$). Two regions that overlap were assumed. The agreement between the experimental $I-U$ curve and the computed one is good at 0°. The systematic deviations for $U > 0.28$ V which are relatively small at 0° become more pronounced with increasing temperature and are considerable at 70°. The experimental curve tends to lie below the computed one in the region between the two current peaks. In general, the computed partial $I-U$

curves for the two regions are wider than the experimental curves. The Langmuir approximation is acceptable in the limited temperature range of 0°–20°. The compensatory effect that leads to a value of $\Delta g_0$, which is nearly independent of partial coverage inside each region, holds between 0° and 20°.

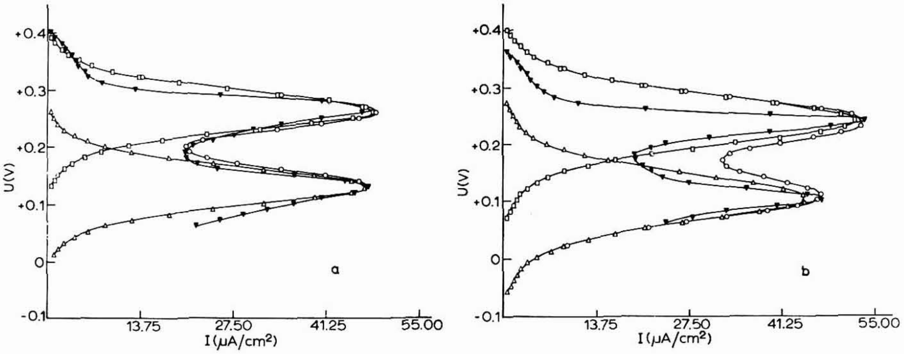

Fig. 1. Experimental $I-U$ curves and curves computed under the assumption of a Langmuir isotherm: (a), 0°; (b), 70°; ▼, experimental curve; ○, computed net curve; △, partial curve for the weakly bonded hydrogen; □, partial curve for the strongly bonded hydrogen.

FRUMKIN ISOTHERM

The parameter $\beta$ in the Frumkin isotherm allows adjustment for the width of the partial $I-U$ curves. Suitable values for $\beta_i$ were chosen to achieve a good approximation to the experimental data. Figures 2(a) and (b) show the computed and the experimental $I-U$ curves at 0° and 70°, respectively. The $I-U$ curves can be approximated better at $T \geqslant 10°$ with Frumkin's than with Langmuir's isotherm. However, $\beta_i$ was not independent of temperature. The values $\beta_1 = 0$ for the weakly bonded hydrogen and $\beta_2 = 0.5$ for the strongly bonded hydrogen were used at $T = 0°$ and $\beta_1 = 0.3$ and $\beta_2 = 1$ at $T = 70°$. In addition, a small third region whose ex-

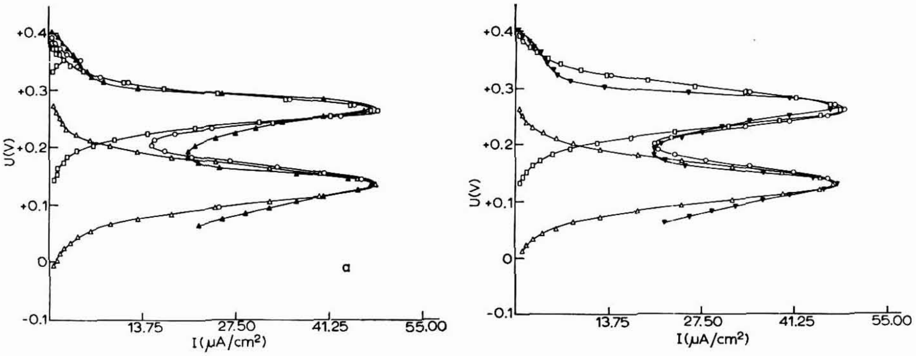

Fig. 2. Experimental $I-U$ curves and curves computed under the assumption of a Frumkin isotherm: (a), 0°; (b), 70°; ▲, experimental curve; ○, computed net curve; △, partial curve for the weakly bonded hydrogen; □, partial curve for the strongly bonded hydrogen; ■, partial curve for the region between 0.37 V and 0.30 V.

istence is indicated by the experimental $I-U$ curve at 0° between 0.37 and 0.30 V was assumed with $\beta_3 = 1$ in the whole temperature range (see Fig. 2(a)). The contribution of this region is negligible at $T > 20°$. The largest deviations between experimental and computed curves occur in the region between the two peaks. It was not possible to improve the fit further than in Figs. 2(a) and (b) with Frumkin's isotherm.

Equation (10) implies that the free energy of adsorption changes with coverage. A positive value of $\beta$ as was found here for the strongly bonded hydrogen corresponds to a decrease of the free energy of adsorption with increasing coverage. The adsorption isotherm is steeper than the corresponding Langmuir isotherm. In the case of physical adsorption, a positive $\beta$-value reflects a tendency towards condensation of the adsorbed film. Since chemisorption is involved here the positive $\beta$-value may be interpreted better as a tendency towards hydride formation. This tendency becomes greater with increasing temperature and is observable at $T > 50°$ for the weakly bonded hydrogen also.

## ACKNOWLEDGEMENT

The author gratefully acknowledges the advice of BRUCE MCCARROLL in the programming.

## SUMMARY

The applicability of a Langmuir type isotherm and of a Frumkin type isotherm to each of the different regions of hydrogen adsorption on smooth platinum in 1 $N$ $H_2SO_4$ was tested between 0° and 70° by comparing experimental and computed current–potential curves at anodic potentials in the region of hydrogen adsorption. The values of the parameters used in the computation were taken from the experimental data. While the Langmuir isotherm yields acceptable results only for $T < 20°$, the Frumkin isotherm allows an approximation in the studied temperature range. The decrease of the free energy of adsorption with coverage for the strongly bonded hydrogen in the studied temperature range and for the weakly bonded hydrogen at $T > 50°$ is interpreted as a tendency to hydride formation.

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# THE POLAROGRAPHY OF *trans*-DINITROBIS(ETHYLENEDIAMINE)-COBALT(III) ION IN BUFFERED SOLUTIONS

## THE MECHANISM OF THE FORMATION OF THE DOUBLE WAVE*

JOHN G. MASON** AND RICHARD L. WHITE

*Departments of Chemistry, Illinois Institute of Technology, Chicago, Ill. and Virginia Polytechnic Institute, Blacksburg, Va. (U.S.A.)*

(Received August 12th, 1964)

## INTRODUCTION

In the course of an investigation of the effect of *cis* and *trans* isomerism on the polarographic reduction potentials of certain cobalt(III) co-ordination compounds, HOLTZCLAW AND SHEETZ[1] reported that in neutral unbuffered potassium chloride a double wave was obtained for the reduction of cobalt(III) to cobalt(II). The total wave height was proportional to the concentration of the particular complex. Both waves were irreversible and although the half-wave potential of the first wave was dependent upon the particular complex being reduced, the half-wave potential of the second wave was essentially the same for the series of co-ordination compounds investigated. From the agreement of the half-wave potential of the second wave with the measured half-wave potential of the di-aquobis(ethylenediamine)cobalt(III) ion, they concluded that the second wave was due to the reduction of a cobalt complex produced by slow aquation of the parent compound.

Cobalt(III) co-ordination compounds are usually *inert* according to the classification of TAUBE[2] while complexes of cobalt(II) are *labile*. When the cobalt complexes are reduced polarographically their character changes since cobalt(II) is in labile equilibrium with its surroundings. Consequently, for those complexes containing ethylenediamine as a ligand, the amount of ethylenediamine released, the interfacial pH, and the distribution of the various possible cobalt(II) species are functions of the current. In the absence of adequate buffering, polarographic waves of electroactive species which are reversible with respect to the electron transfer reaction will have an irreversible shape[3]. Conclusions concerning reversibility should not, therefore, be drawn from data obtained without the use of buffers.

From those complexes studied by HOLTZCLAW AND SHEETZ, which produced the double wave, but which did not aquate rapidly enough to account for the height of the second wave, *trans*-$[Co(en)_2(NO_2)_2]^+$ was selected for further study. Preliminary experiments showed that the height of the first wave was pH-dependent and that the addition of acid or base to a given solution immediately changed the wave height,

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* Taken in part from the M. S. thesis of R. L. White, Virginia Polytechnic Institute, 1962.

** Present address: Department of Chemistry, Virginia Polytechnic Institute, Blacksburg, Virginia, U.S.A.

implying a rapid reversible reaction involving hydrogen ions and not a slow aquation step. Spectrophotometric investigation revealed no significant changes in the spectrum of *trans*-$[Co(en)_2(NO_2)_2]^+$ when the pH was varied or the complex allowed to stand for several hours. These results indicated that the reactions producing the double wave were occurring at the electrode surface and not in the bulk of the solution. A quantitative study of the relation of pH to the height of the first wave was therefore initiated.

## EXPERIMENTAL

### *Reagents and solutions*

*Trans*-$[Co(en)_2(NO_2)_2]NO_3$ was prepared by the method of HOLTZCLAW *et al.*[4]. The product was recrystallized twice from water. The resulting crystals were washed with ice-cold methanol and dried in air. The percentage composition calculated for $C_4H_{16}O_7N_7Co$ is C, 14.42; H, 4.84; N, 29.44. That found on analysis was C, 14.66; H, 4.24; N, 29.39%.

All other reagents were reagent-grade and used without further purification, with the exception of boric acid which was recrystallized in order to obtain reproducible polarograms.

The solutions were prepared by appropriate dilution from stock solutions. The final ionic strength of all solutions was 0.2 *M* with the exception of those used in the nitrite variation where the final ionic strength was 0.3 *M*. Potassium chloride was used in addition to the buffer components for ionic strength adjustment.

### *Polarographic measurements*

Polarograms were obtained using a Leeds and Northrup Electro-Chemograph Type E. A standard polarographic H-cell was used with the S.C.E. in one branch and a bridge solution of 3% agar-saturated potassium chloride. The solutions were outgassed for 20 min with nitrogen purified by the method of MEITES AND MEITES[5]. No maximum supressor was used since maxima were not observed until very high pH values were reached, in spite of reports to the contrary[1].

Several different capillaries were used in the course of this work without affecting the results. Two capillaries with the characteristics 0.963 $mg^{2/3}\,sec^{-1/2}$ and 3.57 $mg^{2/3}\,sec^{-1/2}$ for $m^{2/3}\,t^{1/6}$ measured at open-circuit were used for most of the results. The height of the mercury column was held at 30 cm and the cell was usually kept at 25 ± 0.1° in a thermostat.

A Beckman model G pH meter was used for the determination of pH.

## RESULTS

The effect of changes in pH, concentration of complex, and concentration of nitrite ion were investigated in some detail.

### *Effect of pH*

The importance of the pH in determining the relative wave heights of the first and second waves is shown in Fig. 1. A single wave is observed in sufficiently acidic solutions and a plot of $E$ *vs.* $\log (i_d - i)/i$ yields values of the slope in the range 0.057–0.063. This compares quite well with the theoretical value of 0.059 for a reversible one-electron reduction.

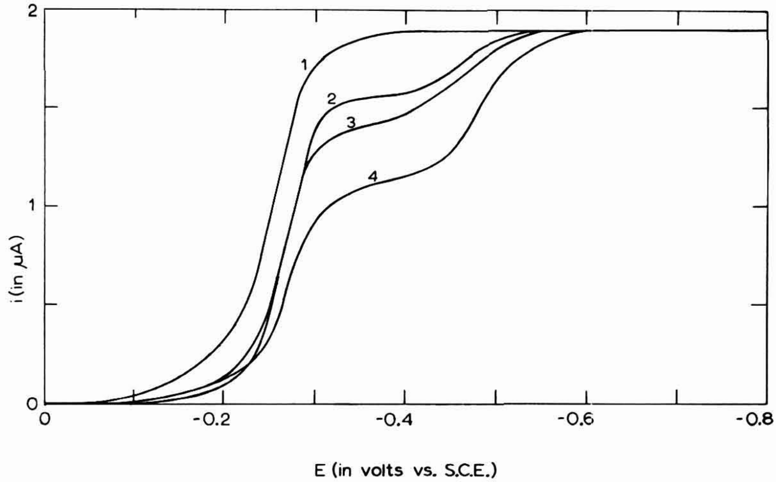

Fig. 1. Dependence of polarogram of 0.001 *M trans*-$[Co(en)_2(NO_2)_2]^+$ on pH: (1), 6.70; (2), 8.95; (3), 9.40; (4), 10.30.

TABLE 1

THE EFFECT OF CHANGES OF pH ON THE REDUCTION OF 0.001 *M trans*-$[Co(en)_2(NO_2)_2]NO_3$ IN 0.2 *M* PHOSPHATE BUFFER

| *pH* | *First wave* | | | *Second wave* | | | $\frac{i_{d_1}}{i_{d_T}}$ |
|---|---|---|---|---|---|---|---|
| | $E_{\frac{1}{2}}$ *(V)* | $i_1$ *(μA)* | *Slope* | $E_{\frac{1}{2}}$ *(V)* | $i_d$ *(total) (μA)* | *Slope* | |
| 5.78 | −0.265 | 4.29 | 0.0625 | — | — | — | — |
| 6.69 | −0.265 | 4.34 | 0.0620 | — | — | — | — |
| 8.20 | −0.267 | 4.19 | 0.0630 | — | — | — | — |
| 9.25 | −0.263 | 3.60 | 0.0620 | −0.466 | 4.13 | 0.0600 | 0.872 |
| 19.60 | −0.262 | 3.04 | 0.0595 | −0.462 | 4.06 | 0.0595 | 0.749 |
| 10.14 | −0.260 | 3.08 | 0.0610 | −0.472 | 4.30 | 0.0585 | 0.716 |
| 10.52 | −0.267 | 2.93 | 0.0595 | −0.489 | 4.20 | 0.0610 | 0.697 |
| 10.69 | −0.264 | 2.96 | 0.0630 | −0.497 | 4.26 | 0.0605 | 0.694 |
| 11.27 | −0.269 | 2.84 | 0.0575 | −0.516 | 4.20 | 0.0600 | 0.676 |

TABLE 2

THE EFFECT OF CHANGES IN pH ON THE REDUCTION OF 0.001 *M* $[Co(en)_2(NO_2)_2]NO_3$ IN 0.2 *M* BORATE BUFFER

| *pH* | *First wave* | | | *Second wave* | | | $\frac{i_{d_1}}{i_{d_T}}$ |
|---|---|---|---|---|---|---|---|
| | $E_{\frac{1}{2}}$ *(V)* | $i_1$ *(μA)* | *Slope* | $E_{\frac{1}{2}}$ *(V)* | $i_d$ *(total) (μA)* | *Slope* | |
| 7.15 | −0.260 | 4.06 | 0.0610 | — | — | — | — |
| 8.82 | −0.260 | 3.16 | 0.0617 | −0.372 | 4.10 | 0.0605 | 0.770 |
| 9.45 | −0.265 | 2.81 | 0.0608 | −0.405 | 4.08 | 0.0598 | 0.690 |
| 9.50 | −0.268 | 2.63 | 0.0625 | −0.414 | 4.05 | 0.0625 | 0.650 |
| 10.40 | −0.266 | 2.31 | 0.0610 | −0.412 | 4.04 | 0.0615 | 0.564 |
| 10.42 | −0.266 | 2.29 | 0.0610 | −0.422 | 4.06 | 0.0620 | 0.564 |
| 10.45 | −0.260 | 2.27 | 0.0600 | −0.430 | 4.06 | 0.0600 | 0.560 |
| 11.10 | −0.265 | 2.20 | 0.0605 | −0.435 | 4.08 | 0.0610 | 0.540 |

The results obtained from the pH variations are given in Tables 1 and 2. It can be seen that $E_{\frac{1}{2}}$ of the first wave is independent of pH and substantially reversible in-so-far as the slope analysis is concerned. The half-wave potential of the second wave which starts to emerge at pH 9 is dependent upon pH and the medium. These results suggest reversibility, although at lower concentrations of the complex, the polarographic wave is irreversible in shape. In all solutions the total wave height is independent of pH. Figure 2 shows the effect of pH on the relative height of the first wave.

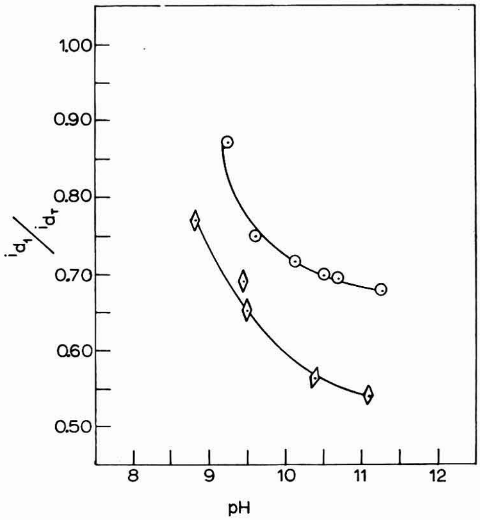

Fig. 2. Relation of height of the first wave to total wave height as a function of pH: ◇, borate; ⊙, phosphate.

*Effect of concentration*

In all cases, the total wave height was found to be proportional to the concentration of complex. In solutions of pH ~ 10, both the height of the first wave and the $E_{\frac{1}{2}}$ of the second were functions of the concentration. In the concentration region $1 \cdot 10^{-4}\,M - 5 \cdot 10^{-4}\,M$ very poor wave separation was achieved and analysis was impossible. At concentrations greater than $5 \cdot 10^{-4}\,M$, well-defined waves appeared. $E_{\frac{1}{2}}$ of the first wave was independent of concentration, $E_{\frac{1}{2}}$ of the second wave became more negative, and the relative height of the first wave, $i_{d_1}/i_{d_T}$, decreased. The effect of changing the concentration at constant pH is similar to that observed on varying the pH at a constant concentration of complex.

*Effect of nitrite ion concentration*

Tables 3 and 4 give the results obtained by varying the $NO_2^-$ concentration in solutions of constant pH. Figure 3 shows a plot of $E_{\frac{1}{2}}$ *vs.* $\log(NO_2^-)$ for borate solutions. The equation for the linear portion of the plot is $E = -0.427 - 0.064 \log[NO_2^-]$. These results are not completely reliable because (i) the correct diffusion

TABLE 3

THE EFFECT OF CHANGES IN NITRITE CONCENTRATION ON THE REDUCTION OF 0.001 *M* *trans*-$[Co(en)_2(NO_2)_2]NO_3$ IN 0.2 *M* PHOSPHATE BUFFER, pH 10.4

| $[NO_2^-]$ *(M)* | *First wave* | | | *Second wave* | | | $\frac{i_{d_1}}{i_{d_T}}$ |
|---|---|---|---|---|---|---|---|
| | $E_{\frac{1}{2}}$ *(V)* | $i_1$ *(μA)* | *Slope* | $E_{\frac{1}{2}}$ *(V)* | $i_d$ *(total) (μA)* | *Slope* | |
| 0 | −0.260 | 2.69 | 0.0615 | −0.476 | 4.04 | 0.0610 | 0.664 |
| 0.001 | −0.264 | 2.68 | 0.0625 | −0.469 | 4.04 | 0.0600 | 0.663 |
| 0.010 | −0.299 | 2.72 | 0.0791 | −0.481 | 4.09 | 0.0615 | 0.665 |
| 0.020 | −0.318 | 2.68 | 0.0845 | −0.480 | 4.07 | 0.0605 | 0.660 |
| 0.050 | −0.345 | 2.65 | 0.0873 | −0.470 | 4.02 | 0.0630 | 0.659 |
| 0.070 | −0.363 | 2.73 | 0.0887 | −0.482 | 4.04 | 0.0705 | 0.675 |
| 0.100 | −0.408 | 4.08 | — | — | — | — | 1.000 |

TABLE 4

THE EFFECT OF CHANGES IN NITRITE CONCENTRATION ON THE REDUCTION OF 0.001 *M* $[Co(en)_2(NO_2)_2]$-$NO_3$ IN 0.2 *M* BORATE BUFFER pH 10.4.

| $[NO_2^-]$ *(M)* | *First wave* | | | *Second wave* | | | $\frac{i_{d_1}}{i_{d_T}}$ |
|---|---|---|---|---|---|---|---|
| | $E_{\frac{1}{2}}$ *(V)* | $i_1$ *(μA)* | *Slope* | $E_{\frac{1}{2}}$ *(V)* | $i_d$ *(total) (μA)* | *Slope* | |
| 0 | −0.266 | 2.45 | 0.0651 | −0.412 | 4.34 | 0.0617 | 0.565 |
| 0.001 | −0.270 | 2.48 | 0.0605 | −0.420 | 4.34 | 0.0621 | 0.572 |
| 0.005 | −0.279 | 2.49 | 0.0597 | −0.416 | 4.34 | 0.0600 | 0.574 |
| 0.010 | −0.299 | 2.47 | 0.0602 | −0.422 | 4.35 | 0.0605 | 0.568 |
| 0.020 | −0.313 | 2.41 | 0.0618 | −0.418 | 4.29 | 0.0600 | 0.562 |
| 0.030 | −0.329 | 2.42 | 0.0622 | −0.421 | 4.28 | 0.0602 | 0.566 |
| 0.050 | −0.343 | 2.41 | 0.0598 | −0.422 | 4.30 | 0.0595 | 0.561 |
| 0.070 | −0.354 | 2.42 | 0.0603 | −0.438 | 4.29 | — | 0.564 |

current of the first wave could not be established with certainty and (ii) the range of $NO_2^-$ concentration which could be covered before the two waves merged was small. The $E_{\frac{1}{2}}$ of the second wave is only seriously affected by high concentrations of $NO_2^-$. The value of $i_{d_1}/i_{d_T}$ is independent of $NO_2^-$ within experimental error.

## DISCUSSION

### *Mechanism of the first wave*

The half-wave potential of the first wave has been shown to be independent of pH but dependent upon the concentration of $NO_2^-$. In solutions of borate, a theoretical slope corresponding to a reversible one-electron reduction is realized. A possible mechanism which might explain the $NO_2^-$ variation is

$$[Co(en)_2(NO_2)_2]^+ + 1\ e \rightleftharpoons [Co(en)_2NO_2]^+ + NO_2^-$$

However, in solutions containing only the complex, the equation for the polarographic wave should be $E = E_{\frac{1}{2}} + 0.059 \log (i_d - i)/i^2$. This relationship was not observed and $E$ *vs.* $\log (i_d - i)/i$ plots showed no curvature.

Similarly, ion pair formation between $[Co(en)_2(NO_2)_2]^+$ and $NO_2^-$ must be excluded because the very large formation constant required to fit the data is inconsistent with the low charges involved.

Further, these mechanisms do not take into consideration the decomposition reactions which would be expected to follow the reduction step.

VLČEK[6] has presented a thorough analysis of polarographic waves which involve a reversible reduction followed by a decomposition reaction. For the reaction scheme

$$MX_n + n\,e \rightleftharpoons MX_n^{n-}$$

$$MX_n^{n-} \rightleftharpoons MX_{n-1}^{n-} \ldots MX_p \underset{k_{+p}}{\overset{k_{-p}}{\rightleftharpoons}} MX_{p-1} \ldots M^{n-}$$

where $k_{-p} \gg k_{+p}$, *i.e.* the position of equilibrium favors the decomposition, the equation for $E_{\frac{1}{2}}$ is

$$E_{\frac{1}{2}} = E^\circ + \frac{RT}{2nF} \ln k_{-p}t \, \frac{\beta_p(X)^p}{\sum\limits_p^n \beta_i(X)^i}$$

where $\beta_i = (MX_i)/(M)(X)^i$, $t$ = drop time, $k_{-p}$ = rate constant for the slow step. The polarographic wave which results has a shape corresponding to a reversible reduction involving $n$ electrons. The shift in $E_{\frac{1}{2}}$ with $(X^-)$ is

$$E_{\frac{1}{2}(2)} - E_{\frac{1}{2}(1)} = \frac{RT}{2nF} \ln \left\{\frac{(X^-)_2}{(X^-)_1}\right\}^p + \frac{RT}{2nF} \ln \frac{\sum\limits_p^n \beta_i(X^-)_1{}^i}{\sum\limits_p^n \beta_i(X^-)_2{}^i}$$

A simple dependence on $(X^-)$ is indicated if the first term on the right predominates or if a single species is present in all solutions. The first condition would mean that as $(X^-)$ increases $E_{\frac{1}{2}}$ should become more positive. The second would yield

$$\Delta E_{\frac{1}{2}} = \frac{RT}{2nF} p \ln \frac{(X^-)_2}{(X^-)_1} + \frac{RT}{2nF} \ln \frac{(X^-)_1{}^i}{(X^-)_2{}^i}$$

which reduces to

$$\Delta E_{\frac{1}{2}} = \frac{RT}{2nF} (p-i) \ln \frac{(X^-)_2}{(X^-)_1}; \quad \Delta E_{\frac{1}{2}} = 0.030\,(p-i) \log \frac{(X^-)_2}{(X^-)_1} \text{ at } 25^\circ$$

In order that $E_{\frac{1}{2}}$ becomes more negative as $(X^-)$ increases, $i > p$. The experimental relation for high concentrations of $NO_2^-$ is

$$E_{\frac{1}{2}} = -0.427 - 0.064 \log (NO_2^-)$$

and

$$\Delta E_{\frac{1}{2}} = -0.064 \log \frac{(NO_2^-)_2}{(NO_2^-)_1}$$

From these $(p - i) = 0.064/0.030$, $p - i = 2.1$, and $p \simeq i - 2$.

If the first product is $[Co(en)_2(NO_2)_2]$, then the species involved in the rate-determining step must have $p = 0$, and therefore is $Co(en)_2{}^{2+}$.

The proposed mechanism is

$$[Co(en)_2(NO_2)_2]^+ + 1\,e \rightleftharpoons [Co(en)_2(NO_2)_2], \text{ reversible}$$

$$[Co(en)_2(NO_2)_2] \rightleftharpoons [Co(en)_2NO_2]^+ + NO_2^-, \text{ rapid}$$

$$[Co(en)_2NO_2]^+ \rightleftharpoons Co(en)_2{}^{2+} + NO_2{}^-, \text{ rapid}$$

$$Co(en)_2{}^{2+} \rightarrow \text{products (rate-determining)}$$

The applicable equation for $E_{\frac{1}{2}}$ as a function of $(NO_2{}^-)$ is

$$E_{\frac{1}{2}} = E^\circ - \frac{RT}{2F} \ln [1 + \beta_1 (NO_2{}^-) + \beta_2 (NO_2{}^-)^2]$$

In solutions which do not contain excess $NO_2{}^-$, the $(NO_2{}^-)$ at the electrode surface should be a function of the current and lead to an apparently irreversible wave shape. The experimental finding that $E$ *vs.* $\log (i_d - i)/i$ plots exhibit no curvature simply means that although the $(NO_2{}^-)$ changes during the course of an electrolysis, the term $\ln [1 + \beta_1(NO_2{}^-) + \beta_2(NO_2{}^-)^2]$ does not change rapidly with the changes in $(NO_2{}^-)$. This conclusion is justified by the rather slow change in $E_{\frac{1}{2}}$ with added $NO_2{}^-$ shown in Fig. 3.

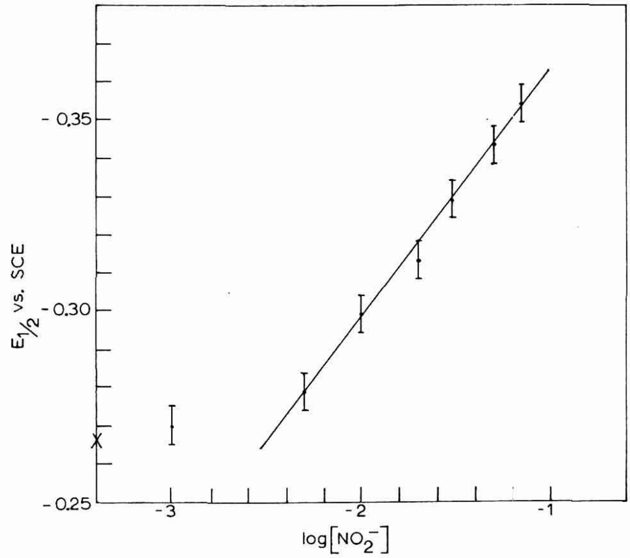

Fig. 3. Effect of nitrite on the $E_{\frac{1}{2}}$ of the first wave in borate buffers, pH = 10.4.

The requirement that $k_{-p} > k_{+p}$ is met in acid solution by the protonation of the ethylenediamine and consequent decomposition of $Co(en)_2{}^{2+}$. In the solutions where the $(NO_2{}^-)$ variation was studied, the reaction for the second wave postulated below serves to favour decomposition although finite amounts of $Co(en)_2{}^{2+}$ can exist in the absence of competing reactions. The dependence of $E_{\frac{1}{2}}$ on $t^{\frac{1}{2}}$ was tested for, but over the range of drop-times studied the results could not be regarded as reliable since the shift is small and the uncertainty in $E_{\frac{1}{2}}$ rather large. However, the trend observed was consistent with that required by the proposed mechanism.

*Mechanism of the second wave*

As the solution becomes more alkaline, a second wave appears. It can be seen in Tables 1 and 2, that the $E_{\frac{1}{2}}$ of the second wave becomes more negative as the pH increases and the height of the second wave increases at the expense of the first. The ratio of the height of the first wave to that of the second approaches unity as a limiting value.

Preliminary experiments ruled out any chemical changes in the bulk of the solution so that the explanation for the appearance of the second wave has to be found in the chemical reactions possible at the drop surface. The possible reaction products if the mechanism proposed for the first wave is correct are, $Co(en)_2^{2+}$, $[Co(en)_2NO_2]^+$, $Co(en)^{2+}$, $[Co(en)_2(NO_2)_2]$ and $Co(en)_3^{2+}$. LAITINEN AND KIVALO[7] reported that in solutions containing aqueous ethylenediamine, the polarographic reduction of $Co(NH_3)_6^{3+}$ yielded a single wave identical to the reduction of $Co(en)_3^{3+}$. They interpreted this result in terms of a ligand exchange reaction in the Co(II) state with subsequent oxidation of the $Co(en)_3^{2+}$ formed to $Co(en)_3^{2+}$. In the region where $Co(NH_3)_6^{3+}$ is reduced, the anodic current cancelled the cathodic current so that the only wave seen ultimately was the anodic wave of $Co(en)_3^{2+}$. LAITINEN AND GRIEB[8] established and KONRAD AND VLČEK confirmed by both potentiometry[9] and polarography[10] that the only oxidizable Co(II)(en) species in this potential region is the $Co(en)_3^{2+}$ ion.

KIVALO[11] found that tris(ethylenediamine)-cobalt(III) was reversibly reduced polarographically and that the apparent irreversibility in solutions containing no excess ethylenediamine was due to the dissociation of tris(ethylenediamine)-cobalt(II) into lower complexes. The changes in wave shape and half-wave potential with pH and the concentration of the complex were consistent with the assumption of reversible electron transfer.

In the polarography of cobalt(III) complexes containing a bis(ethylenediamine) core, reduction produces Co(II) and (en), and makes possible the oxidation of $Co(en)_3^{2+}$. This appears to be the explanation for both the apparent reversibility of the second wave, the pH dependence of $E_{\frac{1}{2}(2)}$ and the decrease in wave height of the first wave while the total diffusion current remains constant.

The net reaction postulated for the second wave is

$$2\ Co(en)_2^{2+} \rightleftharpoons Co(en)_3^{3+} + Co(en)^{2+} + 1\ e$$

Support for this proposal is given by the relation between pH and $i_{d_1}/i_{d_T}$ shown in Fig. 2. If $Co(en)_2^+$ were the electroactive species, then $i_{d_1}/i_{d_T}$ should approach a very small fraction since $i_{d_1}$ would approach the residual current. The limiting value of 0.5 implies the stoichiometry of proposed reaction. Further, the lack of a significant $NO_2^-$ dependence rules out any contribution from a $NO_2^-$ containing species. Calculations using the appropriate formation constants support the finite existence of $Co(en)_3^{2+}$ at the surface of the drop in the pH region under consideration. KONRAD AND VLČEK have observed that in solutions of low concentration of ethylenediamine, a kinetic complication in the anodic wave results from the rate of formation of the $Co(en)_3^{2+}$ complex. The data at hand are insufficient to establish a kinetic factor, however, the values of the $E_{\frac{1}{2}}$ are more positive than the formal potentials for the $Co(en)_3^{2+}$–$Co(en)_3^{3+}$ couple reported by either LAITINEN AND GRIEB (−0.456 V *vs.* S.C.E.), or KONRAD AND VLČEK (−0.446 V *vs.* S.C.E.), which is in the appropriate direction for the half-wave potential of a reaction with partial kinetic control and agrees with the trend in anodic half-wave potentials reported by these investigators.

The lack of influence of the second wave on the shape of the first wave and magnitude of the $E_{\frac{1}{2}}$ for the first wave is supporting evidence for the irreversible step proposed. If all reactions were reversible, then in the pH region where the second wave appears, the shape and slope of the first wave should show a pH dependence.

It is quite surprising that a mixed complex such as *trans*-$[Co(en)_2(NO_2)_2]^+$ has an apparently reversible reduction. However, the major requirement for polarographic reversibility is rapid electron exchange between the oxidized form and the immediate reduction product. In the case of $Co(NH_3)_6^{3+}$ some polarographic reversibility was indicated by the data found[7]. In the case of $Co(en)_3^{3+}$, the reversibility seems to be definitely established. The structure of *trans*-$[Co(en)_2(NO_2)_2]^+$ and the postulated first product, $[Co(en)_2(NO_2)_2]$, would be expected to be quite close with no major structural rearrangement required; hence, low activation energy is needed for the electron exchange. The relative positions of ethylenediamine and $NO_2^-$ in the spectrochemical series suggest that if the $Co(en)_3^{2+}$–$Co(en)_3^{3+}$ couple is reversible, then the $[Co(en)_2(NO_2)_2]$–$[Co(en)_2(NO_2)_2]^+$ couple could be reversible.

## ACKNOWLEDGEMENT

The authors are grateful to the Research Corporation for financial support of this work.

## SUMMARY

The effect of pH and $NO_2^-$ concentration on the polarography of *trans*-$[Co(en)_2(NO_2)_2]^+$ has been studied. The polarographic waves have been interpreted on the basis of the following mechanisms.

Wave I.

$$[Co(en)_2(NO_2)_2]^+ + 1\,e \rightleftharpoons [Co(en)_2(NO_2)_2]$$

$$[Co(en)_2(NO_2)_2] \rightleftharpoons [Co(en)_2(NO_2)]^+ + NO_2^-$$

$$[Co(en)_2NO_2]^+ \rightleftharpoons Co(en)_2^{2+} + NO_2^-$$

$$Co(en)_2^{2+} \xrightarrow{\text{decomposition}}$$

Wave II.

$$2\,Co(en)_2^{2+} \rightleftharpoons Co(en)_3^{3+} + Co(en)^{2+} + 1\,e$$

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# THE POLAROGRAPHIC REDUCTION OF METAL COMPLEXES

C. G. BUTLER AND R. C. KAYE*

*Department of Pharmacy, Institute of Technology, Bradford (England)*

(Received July 21st, 1964)

The interpretation of the polarographic waves of complex metal ions has been discussed by LINGANE[1]. It is pointed out that reduction potentials of metal ions are shifted (usually to more negative values) by complex formation, and that by measuring this shift both the formula and the dissociation constant of the complex can be determined, provided that the reduction of the metal ion is reversible at the dropping mercury electrode. LINGANE's general discussion is restricted to the case where the complexing agent is present in excess, but in considering the case of the incompletely dissociated metal salt, mercury cyanide, he draws attention to the unusual features of the equation of the polarographic wave when the solution does not contain excess cyanide.

This situation bears a close resemblance to that where a metal is present together with an amount of complexing agent just sufficient to form a complex of known composition. An analysis of the relationships involved has been shown to be of value in the interpretation of the polarographic waves of the complex of copper with 8-hydroxyquinoline.

### *Equation of the polarographic wave of the metal*

LINGANE (*loc. cit.*) has considered the case where the reduction of a complex of a metal soluble in mercury may be represented by the net reaction

$$MX_q^{(n-qb)+} + n\,e + \mathrm{Hg} \rightleftharpoons M(\mathrm{Hg}) + qX^{b-}$$

which may for convenience be regarded as the sum of two partial reactions

$$MX_q^{(n-qb)+} \rightleftharpoons M^{n+} + qX^{b-}$$

and

$$M^{n+} + n\,e + \mathrm{Hg} \rightleftharpoons M(\mathrm{Hg})$$

This division is merely an artifice which assists in clarifying the thermodynamic relations involved, and is not intended to indicate an actual kinetic mechanism.

If the above reactions are rapid (compared with diffusion rates) and reversible, the potential of the dropping mercury electrode at any point on the wave should be given by

$$E_{\mathrm{dme}} = \varepsilon + \frac{RT}{nF}\ln\frac{K_c f_{mx}}{f_a (f_x)^q} - \frac{RT}{nF}\ln\frac{C^0{}_a (C^0{}_x)^q}{C^0{}_{mx}} \tag{1}$$

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* Present address: Department of Pharmacology, School of Medicine, Leeds 2.

where

$\varepsilon$ = a constant,

$K_c$ = dissociation constant of the complex,

$C^0{}_a$ = concentration of the metal in the amalgam formed at the electrode surface,

$C^0{}_x$ = concentration of complex-forming ion at the electrode surface,

$C^0{}_{mx}$ = concentration of the metal complex at the electrode surface,

and $f_a, f_x, f_{mx}$ are the corresponding activity coefficients.

In order to express the various concentrations at the electrode surface in terms of the current it is assumed that the diffusion layer is thin and thus the concentration gradients may be considered linear, consequently

$$C^0{}_{mx} = \frac{i_d - i}{k_c} \tag{2}$$

where $i$ is the average current ($\mu$A) during the life of a mercury drop at a given value of $E_{\mathrm{dme}}$, $i_d$ is the limiting diffusion current and $k_c$ is a constant defined by the Ilkovič equation as $k_c = 607\, n D_{mx}{}^{1/2} m^{2/3} t^{1/6}$. $D_{mx}$ is the diffusion coefficient of the complex ($\mathrm{cm^2 sec^{-1}}$), $m$ is the mass of mercury (mg) flowing from the electrode per second and $t$ is the drop time (sec).

Since the concentration of amalgam formed at the surface must be directly proportional to the current

$$C^0{}_a = \frac{i}{k_a} \tag{3}$$

where $k_a$ is defined in the same way as $k_c$ except that the diffusion coefficient of the metal in the amalgam is used.

When the solution contains no excess of complexing agent the concentration of the complex-forming ion at the electrode surface will be proportional to the current and will also depend upon the diffusion coefficients of the complexing agent in its ionized and unionized forms, the dissociation constant of the complexing agent and the pH of the solution. Thus

$$C^0{}_{\bar{x}} k_{\bar{x}} = C^0{}_{h_b x} k_{hx} + C^0{}_x b- \, k_x = qi \tag{4}$$

where $C^0{}_{\bar{x}}$ is the total concentration of complexing agent liberated at the electrode surface, $C^0{}_{h_b x}$ and $C^0{}_x b-$ are the concentrations of unionized and ionized forms and $k$ terms are defined by the Ilkovič equation as before. Since it is unlikely that the $k$ terms will differ greatly in value, eqn. (4) may be re-written

$$C^0{}_{h_b x} + C^0{}_x b- = \frac{qi}{k_{\bar{x}}} \tag{5}$$

If, for convenience, the immediate discussion is restricted to the case of a monobasic acid complexing agent, H$X$, the acid dissociation constant will be given by

$$K_a = \frac{C_h f_h C^0{}_x f_x}{C^0{}_{hx} f_{hx}} \tag{6}$$

and combining this with eqn. (5)

$$C^0{}_x = \frac{qiK_a f_{hx}}{k_{\bar{x}}(C_h f_h f_x + K_a f_{hx})} \tag{7}$$

The values of $C^0{}_{mx}$, $C^0{}_a$ and $C^0{}_x$ given by eqns. (2), (3) and (7) may now be introduced into eqn. (1) and rearranged to give

$$E_{\text{dme}} = \varepsilon + \frac{RT}{nF} \ln \frac{K_c f_{mx} k_a}{f_a k_c} - q \frac{RT}{nF} \ln \frac{q K_a f_{hx} f_x}{C_h f_h f_x + K_a f_{hx}} - q \frac{RT}{nF} \ln \frac{q}{k_{\bar{x}}} - \frac{RT}{nF} \ln \frac{i^{q+1}}{i_d - i} \tag{8}$$

*Reference potential*

In order that eqn. (8) may be used to express the relationship between current and potential in a simple manner it is proposed to define the *reference potential* of the system as that potential at which $\ln i^{q+1}/(i_d - i)$ is zero, the value of $i_d$ being taken as unity (it is necessary to express $i$ as a fraction of $i_d$ on account of the $i^{q+1}$ term). Thus

$$E_{\text{ref}} = \varepsilon + \frac{RT}{nF} \ln \frac{K_c f_{mx} k_a}{f_a k_c} - q \frac{RT}{nF} \ln \frac{K_a f_{hx} f_x}{C_h f_h f_x + K_a f_{hx}} - q \frac{RT}{nF} \ln \frac{q}{k_{\bar{x}}} \tag{9}$$

and the equation of the wave becomes

$$E_{\text{dme}} = E_{\text{ref}} - \frac{RT}{nF} \ln \frac{i^{q+1}}{i_d - i} \tag{10}$$

For a given complex, the term in eqn. (9) which involves the dissociation constant of the complex has a constant value, thus

$$E_{\text{ref}} = E' - q \frac{RT}{nF} \ln \frac{K_a f_{hx} f_x}{C_h f_h f_x + K_a f_{hx}}$$

and from eqn. (10)

$$E_{\text{dme}} = E' - q \frac{RT}{nF} \ln \frac{K_a f_{hx} f_x}{C_h f_h f_x + K_a f_{hx}} - \frac{RT}{nF} \ln \frac{i^{q+1}}{i_d - i} \tag{11}$$

Neglecting activity coefficients, the simplified relation becomes, at 25°.

$$E_{\text{dme}} = E' - \frac{0.0591 q}{n} \log \frac{K_a}{C_h + K_a} - \frac{0.0591}{n} \log \frac{i^{q+1}}{i_d - i} \tag{12}$$

Equation (12) predicts that the polarographic wave of a metal, complexed with $q$ molecules of a monobasic acid of dissociation constant $K_a$ should have the following characteristics in a well-buffered solution and in the absence of excess complexing agent.

(1) Because of the $i^{q+1}$ term, the wave should be unsymmetrical about its midpoint.

(2) A plot of $\log i^{q+1}/(i_d - i)$ against $E_{\text{dme}}$ should give a straight line of slope $0.0591/n$ V at 25°.

(3) The reference potential of the wave will respond to changes in the pH of the solution. Where $C_h$ is small compared with $K_a$, the second term in eqn. (11) is constant, thus $E_{\text{ref}}$ is independent of pH. Where $K_a$ may be neglected compared with $C_h$ a plot of $E_{\text{ref}}$ against pH should yield a straight line of slope $-0.0591\ q/n$ V. The point of intersection of the two straight lines will correspond to pH = p$K_a$.

*Relation between reference potential and half-wave potential of the metal in the presence of excess complexing agent*

Where the complexing agent is present in excess, its concentration at the electrode surface may be taken as equal to that in the bulk solution, and if this value, together with the values of $C^0{}_a$ and $C^0{}_{mx}$ given by eqns. (2) and (3) are introduced into eqn. (1), this becomes, after rearranging

$$E_{\mathrm{dme}} = \varepsilon + \frac{RT}{nF} \ln \frac{K_c f_{mx} k_a}{f_a k_c} - q \frac{RT}{nF} \ln C_x f_x - \frac{RT}{nF} \ln \frac{i}{i_d - i} \tag{13}$$

and the half-wave potential is given by

$$E_{\frac{1}{2}} = \varepsilon + \frac{RT}{nF} \ln \frac{K_c f_{mx} k_a}{f_a k_c} - q \frac{RT}{nF} \ln C_x f_x \tag{14}$$

or, introducing the value of $C_x$ indicated by eqn. (6)

$$E_{\frac{1}{2}} = \varepsilon + \frac{RT}{nF} \ln \frac{K_c f_{mx} k_a}{f_a k_c} - q \frac{RT}{nF} \ln \frac{K_a C_{hx} f_{hx}}{C_h f_h} \tag{15}$$

Combining eqn. (15) with eqn. (9) gives

$$E_{\frac{1}{2}} - E_{\mathrm{ref}} = q \frac{RT}{nF} \ln \frac{C_h f_h f_x}{C_{hx} C_h f_h f_x + K_a C_{hx} f_{hx}} - q \frac{RT}{nF} \ln \frac{k_{\bar{x}}}{q}$$

and since $K_a C_{hx} f_{hx} = C_x f_x C_h f_h$ this simplifies to

$$E_{\frac{1}{2}} - E_{\mathrm{ref}} = q \frac{RT}{nF} \ln \frac{1}{C_{hx} + C_x} - q \frac{RT}{nF} \ln \frac{k_{\bar{x}}}{q} \tag{16}$$

$C_{hx} + C_x$ is the total concentration (mmoles/l) of the free complexing agent in both ionized and non-ionized forms. It may be noted that the relationship given by this equation is independent of the values of activity coefficients.

Equation (16) may be rearranged to give, at 25°

$$-E_{\frac{1}{2}} = 0.0591 \frac{q}{n} \log C_{\mathrm{tot}} + 0.0591 \frac{q}{n} \log \frac{k_{\bar{x}}}{q} - E_{\mathrm{ref}} \tag{17}$$

It is clear from eqn. (17) that a plot of $-E_{\frac{1}{2}}$ against $\log C_{\mathrm{tot}}$ ($C_{\mathrm{tot}} = C_{hx} + C_x$) should give a straight line of slope 0.0591 $q/n$ V, and that if this be extrapolated to $\log C_{\mathrm{tot}} = 0$

$$E_{\mathrm{ref}} - E_{\frac{1}{2}} = 0.0591 \frac{q}{n} \log \frac{k_{\bar{x}}}{q} \tag{18}$$

$$C_{\mathrm{tot}} = 1$$

This relationship gives rise to a novel method for the determination of the Ilkovič constant, $k_{\bar{x}}$ of the complexing ion, and thus its diffusion coefficient.

## *Dibasic acid complexing agents*

If the complexing agent is a dibasic acid, which ionizes in accordance with the equations

$$H_2Y \rightleftharpoons H^+ + HY^-$$

and

$$HY^- \rightleftharpoons H^+ + Y^{2-}$$

the corresponding acid dissociation constants will be given by

$$K_1 = \frac{C_h f_h C_{hy} f_{hy}}{C_{h2y} f_{h2y}} \quad \text{and} \quad K_2 = \frac{C_h f_h C_y f_y}{C_{hy} f_{hy}}$$

The concentration of complexing ion at the electrode surface may again be evaluated and introduced into eqn. (1), which gives the equation of the wave as

$$E_{\mathrm{dme}} = \varepsilon + \frac{RT}{nF} \ln \frac{K_c f_{my} k_a}{f_a k_c} - q \frac{RT}{nF} \ln \frac{K_1 K_2 f_y f_{h_2y} f_{hy}}{C_h{}^2 f_h{}^2 f_y f_{hy} + K_1 C_h f_h f_y f_{h_2y} + K_1 K_2 f_{h_2y} f_{hy}} - q \frac{RT}{nF} \ln \frac{q}{k_{\bar{y}}} - \frac{RT}{nF} \ln \frac{i^{q+1}}{i_d - i} \qquad (19)$$

which at 25° may be simplified to

$$E_{\mathrm{dme}} = E' - \frac{0.0591q}{n} \log \frac{K_1 K_2}{C_h{}^2 + K_1 C_h + K_1 K_2} - \frac{0.0591}{n} \log \frac{i^{q+1}}{i_d - i} \qquad (20)$$

The predictions of eqn. (20) are similar to those of eqn. (12), but a plot of the reference potential with pH should consist of three intersecting straight lines. The relationship between reference potential and half-wave potential with excess complexing agent present is unchanged (eqn. (17)).

With a tribasic acid complexing agent the situation is similar, the simplified equation for the wave, at 25°, being given by

$$E_{\mathrm{dme}} = E' - \frac{0.0591q}{n} \log \frac{K_1 K_2 K_3}{C_h{}^3 + K_1 C_h{}^2 + K_1 K_2 C_h + K_1 K_2 K_3} - \frac{0.0591}{n} \log \frac{i^{q+1}}{i_d - i} \qquad (21)$$

*Reduction from one complexed oxidation state to another*

LINGANE (*loc. cit.*) has shown that where the reaction may be represented by the equation

$$MX_q{}^{(a-qb)+} + n\,e \rightleftharpoons MX_r{}^{(a-n-rb)+} + (q-r)X^{b-} \qquad (22)$$

the potential of the dropping mercury electrode is given by

$$E_{\mathrm{dme}} = E_o - \frac{RT}{nF} \ln \frac{K_{\mathrm{red}} f_{m''x}}{K_{\mathrm{ox}} f_{m'x}} - \frac{RT}{nF} \ln \frac{C^0{}_{m''x}}{C^0{}_{m'x}} - (q-r) \frac{RT}{nF} \ln C^0{}_x f_x \qquad (23)$$

where $E_0$ is the standard potential of the reaction $M^{a+} + n\,e \rightleftharpoons M^{(a-n)+}$, $K_{\mathrm{red}}$ and $K_{\mathrm{ox}}$ are the stability constants of the two complexes, $C^0{}_{m'x}$ is the concentration of oxidised form ($M^{a+}$) at the electrode surface, $C^0{}_{m''x}$ that of the reduced form and $C_x{}^0$ that of the complexing ion. By analogy with eqns. (2), (3) and (7) the concentration terms may be replaced by $C^0{}_{m'x} = (i_d - i)/k_{c'}$

$$C^0{}_{m''x} = \frac{i}{k_{c''}} \quad \text{and} \quad C^0{}_x = \frac{(q-r)i\,K_a f_{hx}}{k_{\bar{x}}(C_h f_h f_x + K_a f_{hx})}$$

(where H$X$ is a monobasic acid) and if these values are introduced into eqn. (23) the equation of the wave is given by

$$E_{\mathrm{dme}} = E_o - \frac{RT}{nF} \ln \frac{K_{\mathrm{red}} f_{m''x} k_{c'}}{K_{\mathrm{ox}} f_{m'x} k_{c''}} - (q-r) \frac{RT}{nF} \ln \frac{q-r}{k_{\bar{x}}} - (q-r) \frac{RT}{nF} \ln \frac{K_a f_{hx} f_x}{(C_h f_h f_x + K_a f_x)} - \frac{RT}{nF} \ln \frac{i^{(q-r+1)}}{i_d - i} \qquad (24)$$

This may be simplified at 25° to

$$E_{\text{dme}} = E' - \frac{0.0591(q-r)}{n}\log\frac{K_a}{C_h + K_a} - \frac{0.0591}{n}\log\frac{i^{(q-r+1)}}{i_d - i} \qquad (25)$$

when the reference potential is given by

$$E_{\text{ref}} = E' - \frac{0.0591(q-r)}{n}\log\frac{K_a}{C_h + K_a}$$

Equation (25) is similar to eqn. (12) and its predictions are similar to those previously discussed.

## EXPERIMENTAL

A preliminary experimental examination has been carried out to investigate the validity of some of the relationships introduced by the equations now presented.

Polarograms were obtained from solutions containing $2 \cdot 10^{-4} M$ $Cu^{2+}$ and $4 \cdot 10^{-4} M$ 8-hydroxyquinoline (*i.e.*, the complex $CuOx_2$) in buffer electrolytes with 50% of dimethylformamide as co-solvent. Dimethylformamide was included in order to increase the solubility of the complex, which is almost insoluble in water. Although in some cases the copper wave was distorted by a maximum (Fig. 1), it was possible to obtain values of the reference potential, and the variation of this with pH* is shown in Fig. 2, where the equation of the line is given by $E = 0.125 - 0.058$ pH V.

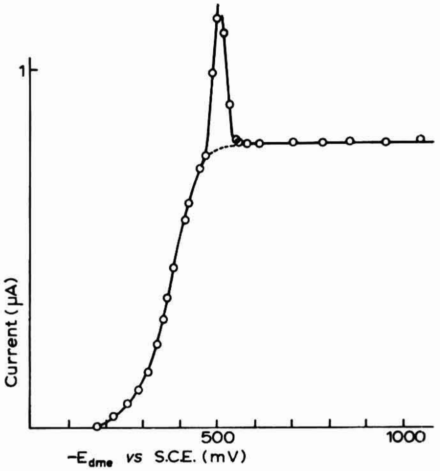

Fig. 1. Polarographic reduction wave of Cu(II) present as its oxine complex in phosphate buffer, pH 7.38, containing 50% of dimethylformamide.

Comparison of these results with eqn. (12) indicates that $n$ is equal to $q$, and the value of $n$ was independently confirmed as 2 by coulometric measurement. In more

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* "pH values" in this instance have been obtained by measurement of the e.m.f. of the cell $Pt|H_2(1\ atm)|solution||KCl(aq.sat.)|Hg_2Cl_2|Hg$ and the application of the relationship "pH" = $(E - E^0{}_{\text{cal}})F/2.303\ RT$ as recommended by GUTBEZAHL AND GRUNWALD[3]. No account was taken of the unknown liquid junction potential, which was assumed to be constant with unchanged solvent composition.

alkaline solutions the reduction becomes pH-independent, with the "p$K$ bend" at pH 11.3 indicating that the acid dissociation constant for oxine in this medium[3] is equal to $10^{-11}$.

In order to test the remaining (current) term of eqn. (12) it was necessary to obtain waves reasonably free from distortion in order to apply logarithmic analysis.

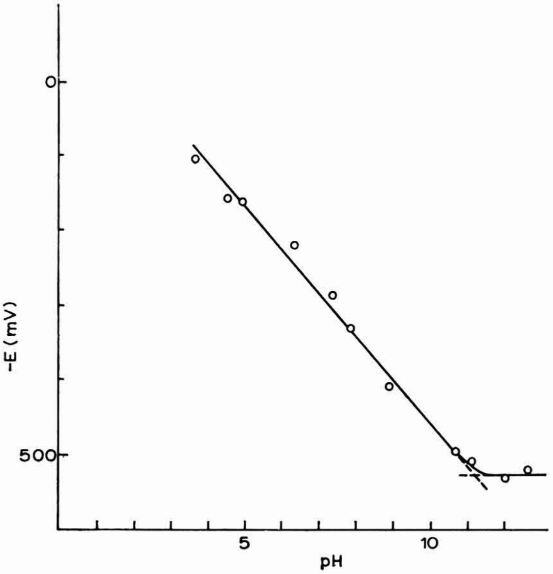

Fig. 2. Variation of reference potential of oxine-complexed Cu(II) with pH.

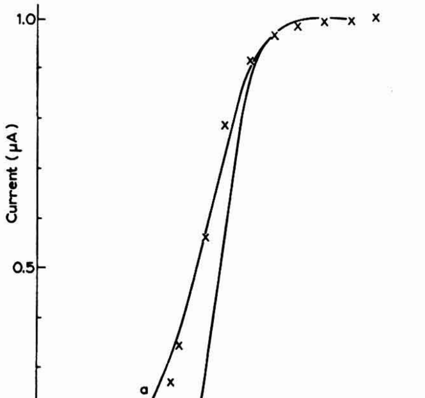

Fig. 3. Polarographic reduction wave of Cu(II) complex with oxine-5-sulphonic acid: (×), experimental points; (a) and (b), theoretical curves of the equations given in the text.

The dimethylformamide concentration was lowered to 30% and the oxine replaced by oxine 5-sulphonic acid, the copper complex of which is more soluble in water.

Figure 3 shows theoretical waves for the equations

$$E_{\text{dme}} = E_{\text{ret}} - \frac{0.0591}{n} \log \frac{i^3}{i_d - i} \tag{a}$$

and

$$E_{\text{dme}} = E_{\frac{1}{2}} - \frac{0.0591}{n} \log \frac{i}{i_d - i} \tag{b}$$

together with the experimental points in the polarographic reduction of a solution containing $4 \cdot 10^{-4}$ $M$ copper complex of oxine 5-sulphonic acid. Logarithmic analysis (plot of log $i^3/(i_d - i)$ against $E_{\text{dme}}$) of the experimental curve gave the results shown in Fig. 4.

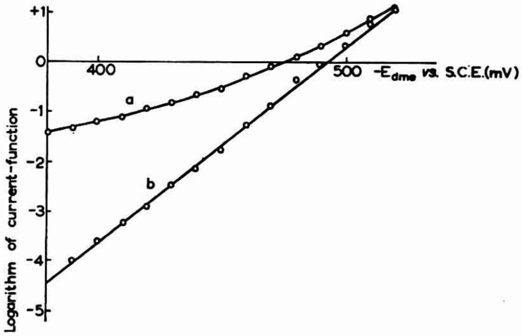

Fig. 4. Logarithmic analysis of polarographic wave of Cu(II) complex with oxine-5-sulphonic. (a), log $i/(i_d - i)$ against $E_{\text{dme}}$; (b), log $i^3/(i_d - i)$ against $E_{\text{dme}}$.

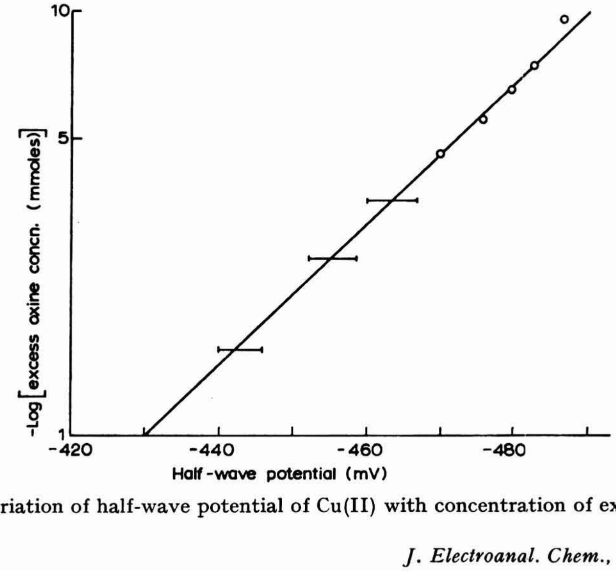

Fig. 5. Variation of half-wave potential of Cu(II) with concentration of excess oxine.

The slope of 26 mV per log unit confirms an $n$-value of 2. A plot of $\log i/(i_d - i)$ for this wave is included for comparison.

In order to test eqn. (17) polarograms were obtained of solutions in 50% aqueous-dimethylformamide buffer (pH 8.9) of $2 \cdot 10^{-4}\,M$ $Cu^{2+}$ with amounts of oxine varying from $4 \cdot 10^{-4}\,M$ to $10^{-2}\,M$. The half-wave potentials were plotted against excess of oxine using semi-logarithmic paper (Fig. 5). The line has a slope of 0.061 V, again indicating that $n = q$. At millimolar excess of oxine, $E_{\frac{1}{2}}$ is equal to −0.430 V. The reference potential of $2 \cdot 10^{-4}\,M$ copper oxinate in this buffer was found to be −0.411 V, and from eqn. (18) $k_{\bar{x}}$ was found to be equal to 4.3. Introduction of this value into the Ilkovič equation gave the diffusion coefficient for oxine in this electrolyte as $D = 2.9 \times 10^{-6}$ cm$^2$sec$^{-1}$. Direct polarographic measurement using oxine[2] has yielded a value of $D = 1.2 \times 10^{-6}$ cm$^2$sec$^{-1}$. Agreement is thus not close enough to assess at the present time the value of the method as a means of evaluation of polarographic diffusion coefficients, although it may be pointed out that the ratio of the square roots (*cf.* Ilkovič equation) of the two values is about 1.5 to 1.

## SUMMARY

When a metal, present as the complex $MX_q$, is polarographically reduced in the absence of excess complexing agent the equation of the wave at 25° is given by

$$E_{\text{dme}} = E' - \frac{0.0591q}{n}\log\frac{K_a}{C_h + K_a} - \frac{0.0591}{n}\log\frac{i^{q+1}}{i_d - i}$$

The wave is consequently unsymmetrical about its midpoint and the reduction potential will be pH-dependent over a range of pH depending on the value of $K_a$ (the acid dissociation constant of the complexing agent).

A comparison of the above case with that which applies when complexing agent is present in excess yields a relationship which may lead to the evaluation of the polarographic diffusion coefficient of the complexing ion.

Some supporting experimental evidence is presented.

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# Short Communications

## Phase angle titration: a new electroanalytical technique

When a constant alternating current is applied between two platinum electrodes (one of them being a polarisable micro-electrode, and the other a non-polarisable gauze electrode) immersed in a reversible redox system whose concentration of the reducible constituent varies in the course of a titration, the relative phase angle (between current and voltage) of the titration cell is also found to vary. It is further found that a large change in the relative phase angle of the titration cell, as indicated in the phasemeter, takes place at the end-point in the titration. This titration is known as phase angle titration and is closely related to the impedance titration[1,2] reported earlier.

*Experimental technique*

The experimental arrangment is given in Fig. 1. The phase angle of the titration cell can be measured easily with any good phase angle meter. A constant alternating current of the order of 100 μA was passed between the two platinum electrodes dipped in the solution to be titrated. The phase angle of the titration cell was measured with Dawe's Transistor Phasemeter Type 630. The reference signal was of the same order as the signal from the titration cell and given separately to the reference signal channel of the phasemeter. This enabled the phasemeter to indicate the phase change occurring in the titration cell independent of the a.c. amplitude changes across the cell. The precision of the phase angle meter was enhanced by replacing the indicating meter by a Kipp and Zonen Micro VA AL.4 having an 8 in. dial (range 0–15 μA). Further precision was obtained by bringing the Micro VA meter reading to zero at any desired phase angle and noting the subsequent changes by the indication on the sensitive ranges of the Kipp and Zonen meter. The phase angle changes could thus be measured to an accuracy of 0.25°. A considerable change in the phase

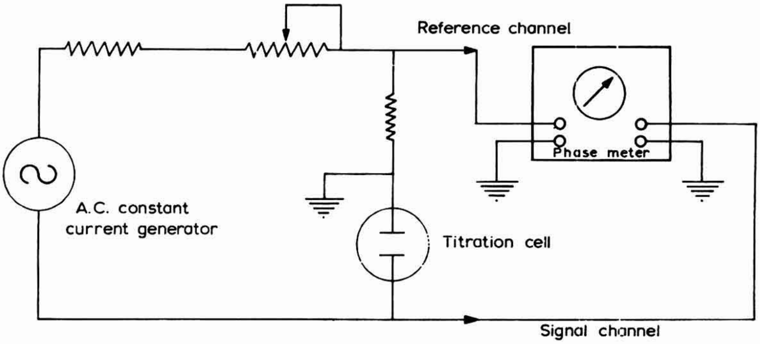

Fig. 1. Experimental arrangement for the phase angle titration.

angle was noticed at the end-point of the titration. The apparent surface area of the platinum microelectrode was 0.1 cm$^2$.

*Results*

The results for (i) titration of ferrous ammonium sulphate against potassium permanganate and (ii) titration of ferrous ammonium sulphate against ceric sulphate are shown in Figs. 2 and 3 respectively. The inset in each case shows the derivative

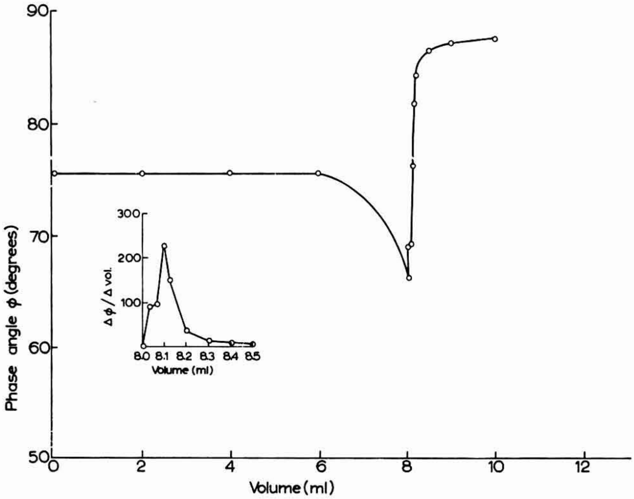

Fig. 2. The curve of phase angle $\phi$ *vs.* volume for the system 0.001 *N* $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ *vs.* 0.001 *N* $KMnO_4$ (a.c., 100 $\mu$A).

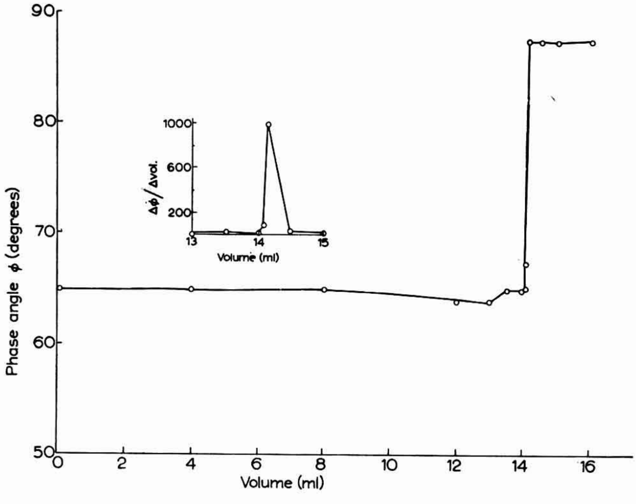

Fig. 3. The curve of phase angle $\phi$ *vs.* volume for the system 0.001 *N* $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ *vs.* 0.001 *N* $Ce(SO_4)_2$ (a.c., 100 $\mu$A).

curve near the end point. Experiments were also conducted using 0.1 *N* and 0.01 *N* solutions. The curves are essentially the same as those obtained in the experiment with the 0.001 *N* solution.

The precision with which the titration can be carried out by this technique is ±0.1% in the case of 0.1 *N* and 0.01 *N* solutions and ±0.2% for 0.001 *N* solutions.

*Discussion*

The equivalent circuit of the titration cell system can be represented by Fig. 4.

The phase angle of the total current (in relation to voltage) is determined mainly by the vectorial sum of the double layer current $i_{dl}$ and Faradaic current $i_f$ since the electrolyte resistance $R_s$ is small. This is represented in Fig. 5 and is expressed by the equation

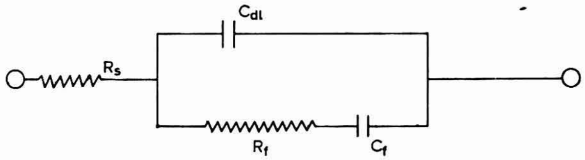

Fig. 4. Equivalent circuit of the titration cell: $R_s$, resistance of the solution; $C_{dl}$, capacitance due to electrical double layer; $R_f$, reaction resistance; $C_f$, pseudo-capacitance.

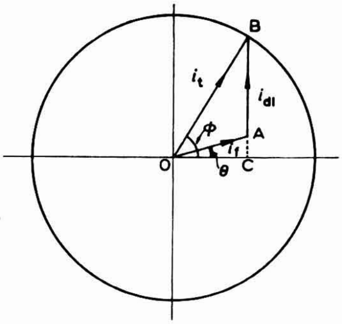

Fig. 5. Vector diagram of the cell current: $i_t$, total current passing through the titration cell; $i_f$, Faradaic current; $i_{dl}$, electrical double-layer current.

$$i_t = i_{dl} + i_f \tag{1a}$$

and

$$i_t \cos \phi = i_f \cos \theta \tag{1b}$$

The magnitude of $i_f$ (Faradaic current) is dependent on the balance of the system. The balance would decrease with the decrease in reversibility of the redox system as well as when $C_O/C_R$ progressively deviates from unity. In view of this, the electrode system containing merely a pure oxidant or reductant would give rise to a negligible $i_f$. Hence, from eqn. (1), the phase angle of the current would therefore be nearly equal to 90°. In the intermediate regions up to just before the equivalence point however, the $C_0$ being comparable with $C_R$, the magnitude of the Faradaic current would be comparable with the total current and hence the phase angle of total current would be much less than 90°.

In Fig. 5, the locus of the points for the total constant current passed through the titration cell is a circle. The phase of the Faradaic current is given by $\cos\theta = i_t \cos\phi / i_f$ and is represented by $\overline{OA}$ with reference to $\overline{OC}$. The current due to the electrical double layer is represented by $\overline{AB}$ and is perpendicular to $\overline{OC}$. $\overline{OB}$ makes an angle $\phi$ with reference to $\overline{OC}$ giving the total phase angle with reference to the reference voltage due to passage of the constant current. As discussed before, the magnitude of $\overline{OA}$ is small compared to $\overline{AB}$ before the start of the titration and also immediately after the equivalent point of the titration, due to the presence of either $C_0$ or $C_R$. During the course of the titration and just before the equivalence point, the magnitude of $\overline{OA}$ is comparable with $\overline{AB}$, with the result the phase angle of the total current would be much less than 90°.

The above expectations are generally fulfilled by the systems studied in this paper. In the beginning of the titration the phase angle is lower than 90° presumably due to the presence of ferric ions in the ferrous solution.

*Acknowledgement*

The authors wish to record their gratitude to Prof. K. S. G. Doss, Director of the Central Electrochemical Research Institute, for his interest in the work.

*Central Electrochemical Research Institute,*
*Karaikudi (India)*

U. H. NARAYANAN
G. DORAIRAJ
Y. MAHADEVA IYER

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Received May 30th, 1964

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# Effect of junction potentials at the salt bridge on the measured values for the half-wave potentials of the $Pb^{2+} \rightarrow Pb^0$ reduction in aqueous solutions of hydrochloric acid and potassium chloride*

Liquid junction potentials are well known in electrochemistry. Because such potentials are difficult to measure accurately, their significance tends to be overlooked. The magnitude of such potentials can be surprisingly large. This communication is a reminder that experimental techniques should be selected carefully so as to minimize their effect.

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* Research sponsored by the U.S. Atomic Energy Commission under contract with the Union Carbide Corporation.

During experimentation to compare the Teflon dropping-mercury electrode (D.M.E.) with the glass D.M.E. for determining polarographic characteristics of redox systems, an observation was made that may be of interest to others working in polarography and controlled-potential coulometry. Data were obtained which indicate that junction potentials at the salt bridge have a significant effect on the measured value for the half-wave potential ($E_{\frac{1}{2}}$) *vs.* S.C.E. of the $Pb^{2+} \rightarrow Pb^0$ reduction, in HCl as supporting medium, whereas for KCl as supporting medium the effect is much smaller. This observation is important in view of the fact that the $E_{\frac{1}{2}}$ values for the $Pb^{2+} \rightarrow Pb^0$ reduction, and also for the $Tl^+ \rightarrow Tl^0$ reduction, are reported to be the same for HCl and KCl as supporting electrolytes[1,2]. Indeed, the values are the same within a few mV if, in the case of each electrolyte, the test solution is bridged to the S.C.E. *via* a saturated solution of KCl. However, for HCl supporting media, salt bridges of different types give measured values of $E_{\frac{1}{2}}$ that differ considerably.

Although the effect was observed experimentally for the $Pb^{2+} \rightarrow Pb^0$ reduction, presumably it will be the same for other reductions when the type and/or concentration of electrolyte in the bridge differ from those in the test solution or in the reference-electrode solution.

The significance of the junction potentials of a particular bridge for a particular supporting electrolyte is a factor to be considered in both qualitative and quantitative polarography. This factor may also be important in controlled-potential coulometry, because the reduction potential required for a certain controlled-potential coulometric determination is often established polarographically and the reference electrode is frequently a S.C.E. bridged to the test solution.

## EXPERIMENTAL

### *Reagents*

All the solutions were prepared from triple distilled water and ACS reagent grade chemicals. Nitrogen or argon, passed through a wash of the supporting medium, was used to deaerate the test solutions and was passed over them during the measurements.

The $1.0 \cdot 10^{-3}$ *M* solutions of $Pb^{2+}$ were prepared by dissolving 69 ± 0.1 mg of dry lead chloride, $PbCl_2$, in 250 ml of the particular supporting medium.

### *Instrumentation and apparatus*

The instrumentation and apparatus were as described elsewhere[3].

The voltage calibration of the X-Y recorder was carefully and frequently checked.

## RESULTS AND DISCUSSION

Table 1 gives a summary of the experimental results that show the effect of junction potentials at the salt bridge on the measured values for $E_{\frac{1}{2}}$ *vs.* S.C.E. of the $Pb^{2+} \rightarrow Pb^0$ reduction in aqueous solutions of HCl and of KCl as supporting electrolyte.

For the HCl supporting media, the $E_{\frac{1}{2}}$ values measured when the salt bridge was a saturated solution of KCl are in very satisfactory agreement with reliable values reported in the literature[1,2]. For the bridge of NaF–agar agar/0.1 *M* KCl, which is being used in some work with the Teflon D.M.E., the measured $E_{\frac{1}{2}}$ of the $Pb^{2+} \rightarrow Pb^0$ reduction in HCl media is about 20–30 mV more negative than that measured when the bridge is a saturated solution of KCl. When the salt bridge is 0.200 *M* $KNO_3$, the

TABLE 1

EFFECT OF JUNCTION POTENTIALS AT THE SALT BRIDGE ON THE MEASURED VALUES FOR $E_{\frac{1}{2}}$ OF THE $Pb^{2+} \rightarrow Pb^0$ REDUCTION IN HCl AND KCl MEDIA

Test solutions: 1 m$M$ $PbCl_2$ in the supporting media indicated.

| *Supporting medium* | | *Solution identity* | *D.M.E.* | *$E_{\frac{1}{2}}$ (V vs. S.C.E. via indicated salt bridge)* | | |
|---|---|---|---|---|---|---|
| *Electrolyte* | *M* | | | *NaF–agar agar \|0.1 M KCl* | *Sat. KCl soln.* | *0.200 M $KNO_3$* |
| HCl[a] | 1.0 | A | Teflon | −0.463 | | |
| | | | Glass | | −0.441[b] | |
| | | B | Teflon | −0.464 | | |
| | | | Glass | | −0.442[b] | −0.497 |
| | | C | Teflon | −0.463 | −0.435[b] | |
| | | | Glass | | −0.442[b] | |
| | 3.0 | | Teflon | −0.533 | | |
| | | | Glass | | −0.503 | |
| | 6.0 | | Teflon | −0.624 | | |
| | | | Glass | | −0.587 | |
| KCl | 1.0 | | Teflon | −0.429 | −0.431[b] | |
| | | | Glass | | −0.435[b] | −0.446 |

[a] The HCl used to prepare the solutions A, B, and C was from different sources.

[b] For this bridge, an accepted $E_{\frac{1}{2}}$ value is −0.435 V *vs.* S.C.E.[1,2].

difference is still greater, *i.e.*, about 50 mV. In HCl media, the junction potentials at the bridge can therefore cause erroneous qualitative and quantitative polarographic and controlled-potential coulometric results. Errors in coulometric results are more likely to occur if several ions are being determined in sequence in the same test solution. For KCl as supporting electrolyte, the type of salt bridge is much less, but still somewhat significant. When accurate values for $E_{\frac{1}{2}}$ *vs.* the S.C.E. are to be measured, the salt bridge should contain either saturated KCl or the supporting medium.

The $E_{\frac{1}{2}}$ values for the three concentrations of HCl are consistent with the known fact that the $E_{\frac{1}{2}}$ of the $Pb^{2+} \rightarrow Pb^0$ reduction becomes more negative as chloride concentration increases[4].

It is not well understood why the junction potentials of the salt bridge are larger for HCl than for KCl as supporting electrolyte. Possibly the difference results from the difference in the mobilities of the hydrogen and potassium ions.

*Analytical Chemistry Division,*
*Oak Ridge National Laboratory,*
*Oak Ridge, Tenn. (U.S.A.)*

W. L. BELEW
HELEN P. RAAEN

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Received July 10th, 1964

# Amperometric titration of zinc with potassium ferrocyanide by a. c. polarography

SPÁLENKA[1] titrated potassium ferrocyanide with zinc in 0.2 *N* HCl solution at a potential of −1.2 V; zinc gave a diffusion current and the product of reaction was found to correspond to $K_2Zn_3[Fe(CN)_6]_2$. NIMER, HAMM AND LEE[2] investigated the direct amperometric titration of zinc with potassium ferrocyanide in a supporting electrolyte of 1.7 *M* ammonium acetate at an applied potential of −1.4 V *vs.* S.C.E. The precipitate formed had the approximate composition $Zn_2[Fe(CN)_6]$. KHOSLA AND GAUR[3] estimated small amounts of zinc with potassium ferrocyanide in acid solution and confirmed the composition of the precipitate as given by SPÁLENKA.

Although a considerable amount of work has been done on amperometric titrations by conventional polarography, there is no data in the literature on the same determination using a.c. polarography. The purpose of the present investigation is, therefore, (i) to ascertain if a.c. polarography can be applied in the estimation of small amounts of zinc by an amperometric titration with potassium ferrocyanide and (ii) to investigate the composition of the precipitate formed.

Pure, recrystallised zinc sulphate ($ZnSO_4 \cdot 7H_2O$) and potassium ferrocyanide (B.D.H., A.R.) were used. Mercury for the dropping electrode was purified by passing it through Meyer's column, after which it was washed several times with distilled water, dried, passed through a sintered-glass filter and finally distilled under vacuum. A known volume of zinc sulphate solution of suitable strength was titrated amperometrically at pH 2.2 and pH 6.8 with a standard solution of potassium ferrocyanide. The titrant was of different strengths, ranging from $2.50 \times 10^{-4}$ *M* to $9.20 \times 10^{-2}$ *M*.

The technique of a.c. polarographic measurements is the same as that described

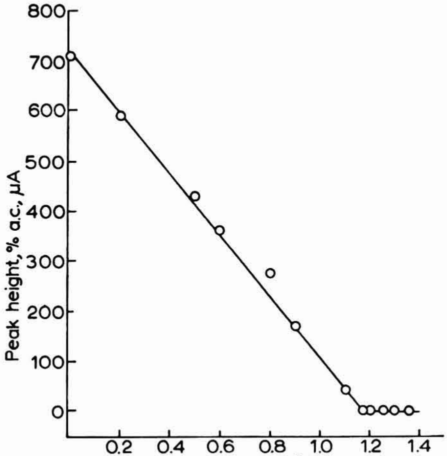

Fig. 1. A.c. amperometric titration on zinc with potassium ferrocyanide; 50.0 ml of $3.15 \times 10^{-3}$ *M* zinc; end-point, 1.17 ml.

earlier[4,5], the only modification being that the series resistance was made as small as possible by applying to the D.M.E., a 50 c/sec a.c. ripple of 20 mV (r.m.s.) on the d.c. potential and observing the alternating component of the resulting pulsating current.

A 0.1 *M* potassium chloride (B.D.H., A.R.) solution in conductivity water was used as the supporting electrolyte. Negative d.c. potentials were applied to the D.M.E. with respect to the saturated calomel electrode. The experiments were carried out at a constant temperature of 30 ± 0.5°. The constants of the D.M.E. were: $m = 4.564$ mg/sec and $t = 1.8$ sec per drop in 0.1 *M* KCl, open circuit. The titrations were carried out at a potential of −1.02 V *vs.* S.C.E. At this voltage, zinc produces a very high a.c. peak whereas $K_4Fe(CN)_6$ is not reducible at the D.M.E.[6].

A typical curve depicting the results obtained by titrating a $3.15 \times 10^{-3}$ *M* solution of zinc with $8.9 \times 10^{-2}$ *M* potassium ferrocyanide solution is given in Fig. 1. Table 1 gives the results obtained at pH 2.2 and Table 2 refers to the same titrations at pH 6.8. It can be seen from column 5 in both the tables that the best results are obtained at lower pH values. It is of interest to note that a clear and distinct end-point could even be obtained in the titration of a dilute solution of zinc, of the order

TABLE 1

$ZnSO_4$ solution = 50.0 ml; pH = 2.2; $E_p$ = −1.02 V *vs.* S.C.E.*

| *Concentration (mole/l)* | | *Titre values (ml)* | | |
|---|---|---|---|---|
| *$ZnSO_4$* | *$K_4Fe(CN)_6$* | *Calc.* | *Obs.* | *Error (%)* |
| $1.57 \times 10^{-3}$ | $4.5 \times 10^{-2}$ | 1.16 | 1.17 | +0.8 |
| $1.62 \times 10^{-3}$ | $4.5 \times 10^{-2}$ | 1.20 | 1.20 | 0 |
| $2.43 \times 10^{-3}$ | $4.5 \times 10^{-2}$ | 1.80 | 1.81 | +0.5 |
| $3.15 \times 10^{-3}$ | $8.9 \times 10^{-2}$ | 1.18 | 1.17 | −0.8 |
| $3.87 \times 10^{-3}$ | $9.2 \times 10^{-2}$ | 1.40 | 1.39 | −0.7 |
| $5.0 \times 10^{-4}$ | $1.5 \times 10^{-2}$ | 1.11 | 1.11 | 0 |
| $2.0 \times 10^{-4}$ | $7.0 \times 10^{-3}$ | 0.95 | 0.94 | −1.0 |
| $5.0 \times 10^{-5}$ | $2.4 \times 10^{-3}$ | 0.69 | 0.70 | +1.4 |
| $2.0 \times 10^{-5}$ | $5.0 \times 10^{-4}$ | 1.33 | 1.32 | −0.7 |
| $1.0 \times 10^{-5}$ | $2.5 \times 10^{-4}$ | 1.33 | 1.32 | −0.7 |

TABLE 2

$ZnSO_4$ solution = 50.0 ml; pH = 6.8; $E_p$ = −1.02 V *vs.* S.C.E.*

| *Concentration (mole/l)* | | *Titre values (ml)* | | |
|---|---|---|---|---|
| *$ZnSO_4$* | *$K_4Fe(CN)_6$* | *Calc.* | *Obs.* | *Error (%)* |
| $1.62 \times 10^{-3}$ | $4.5 \times 10^{-2}$ | 1.2 | 1.26 | +5.0 |
| $2.43 \times 10^{-3}$ | $4.5 \times 10^{-2}$ | 1.8 | 1.7 | −5.5 |
| $1.57 \times 10^{-3}$ | $8.9 \times 10^{-2}$ | 0.59 | 0.64 | +8.4 |
| $3.15 \times 10^{-3}$ | $8.9 \times 10^{-2}$ | 1.18 | 1.22 | +3.3 |
| $3.87 \times 10^{-3}$ | $9.2 \times 10^{-2}$ | 1.4 | 1.45 | +3.5 |

* $E_p$, peak potential.

of $1.0 \times 10^{-5}$ $M$; this is not possible by conventional polarography. The titration figures indicate that the composition of the precipitate formed is essentially $K_2Zn_3[Fe(CN)_6]_2$ whatever the strength of ferrocyanide used.

The amperometric titrations of nickel with ferrocyanide, and lead with oxalate and dichromate have also been studied by a.c. polarography; the details will be published elsewhere.

It may be concluded, therefore, that amperometric titrations in dilute solutions and the composition of the precipitate formed can be successfully investigated using a.c. polarography. The method has the following advantages over the conventional amperometric titration:

(i) concentrations as low as $1.0 \times 10^{-5}$ $M$ can be estimated and the addition of a maximum suppressor is eliminated;

(ii) oxygen need not be removed from the solution;

(iii) measurements can be made more rapidly and with an improved all round reproducibility.

*Acknowledgement*

We are grateful to the Director, Birla Institute of Technology and Science for the interest he showed in this investigation and to the C.S.I.R. (New Delhi) for the award of a Research Fellowship to one of US (S.K.S.)

*Department of Chemistry,*
*Birla Institute of Technology and Science,*
*Pilani, Rajasthan (India)*

S. L. GUPTA
S. K. SHARMA

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Received July 25th, 1964

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# Polarographic determination of silver in gold

Cathodic polarographic waves of silver occur near zero-applied potential *versus* the mercury pool anode in most supporting electrolytes, but the waves are usually not separable from the anodic dissolution wave of mercury. Some investigators[1,3] have used a platinum micro-electrode to avoid interference from electrochemical dissolution of mercury at the dropping mercury electrode. A satisfactory measure of the silver diffusion currents using the dropping mercury electrode may, however, be achieved by comparing the residual current of a blank polarogram with the silver diffusion current (Figs. 1 and 2). In this way the advantages of the dropping mercury electrode are retained.

*J. Electroanal. Chem.*, 8 (1964) 480–482

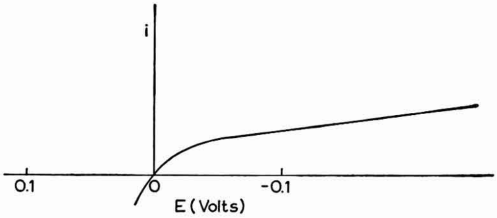

Fig. 1. Blank residual current.

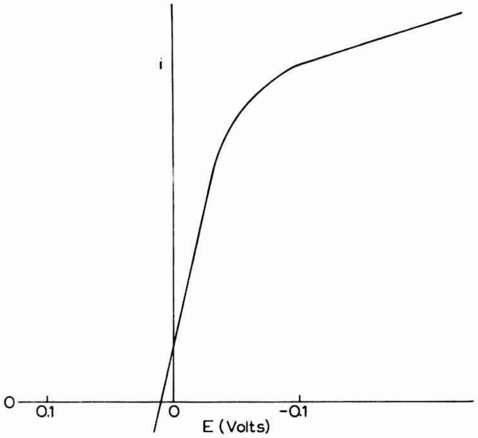

Fig. 2. Silver diffusion current.

In most supporting electrolytes the wave due to reduction of auric gold precedes or coincides with the silver wave. For example, in cyanide or alkaline media the gold wave precedes that of silver. When the gold concentration is more than five times the silver concentration, poor definition of the silver wave results.

Auric gold is reduced to metallic gold in 1 *N* hydriodic acid[4,5] as shown by the appearance of a gold film on the interior surface of the vessel. Interference from gold may thus be eliminated. It is not necessary to separate the liquid phase from the solid phase (gold) since metallic gold is inert and does not interfere in the subsequent steps of the determination.

Hydriodic acid also reacts with the silver in the sample solution forming the complex $Ag_3I_4^-$ (ref. 6). Silver produces a polarographic wave near zero-applied potential when it is thus complexed as the iodide in 1 *N* hydriodic acid.

### *Procedure*

Dissolve the gold–silver alloy containing 100–300 $\mu$g of silver in a minimum volume of ***aqua regia***. When solution is complete, add 2 ml of 47% HI and evaporate to dryness. Add a further 2 ml of 47% HI and evaporate to dryness. Dissolve the salts from the warm beaker with 2 ml of 47% HI and transfer the liquid, with washing, to a 10-ml volumetric flask and dilute to the mark with deionized water.

Transfer to a 10-ml Heyrovský cell, de-oxygenate with nitrogen for 15 min, and blanket with nitrogen. Develop the polarogram from 0 to −0.3 V *vs.* the mercury pool anode. Run a blank on the HI electrolyte to establish the residual current.

Gold may be determined if necessary, by converting auric gold from the dissolution step to the hydroxide complex[2] with 2 *N* KOH supporting electrolyte. The wave of $E_{\frac{1}{2}} = -0.4$ V is used for the determination.

### *Results*

Experimental conditions: temperature, 25°; drop time, 5.0 sec; capillary constant, 1.26.

The diffusion current constant for the silver wave was determined under these conditions, $i = i_d/Cm^{\frac{2}{3}}t^{\frac{1}{6}} = 2.34$.

*Chemistry Department,*
*Honeywell Inc.,*
*Minneapolis, Minn. 55408 (U.S.A.)*

JAMES R. LUCK
E. H. LINDEMAN

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Received August 3rd, 1964

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## The electrode potential of silver and silver–silver halide electrodes

The potentials of Spec-pure silver and silver–silver halide electrodes were measured at 25° in buffered $Cl^-$, $Br^-$ and $I^-$ solutions, over the pH range 1.18–12.32, and the halide concentration range 2 *N* to $10^{-4}$ *N*. The solutions were de-aerated before measurements by stirring with purified nitrogen. The potentials obtained with the silver electrode were satisfactorily reproducible and those obtained with the silver–silver halide electrodes showed remarkable stability with time and were frequently reproducible to the nearest tenth of a millivolt.

Representative $E_H$–p$X$ curves ($X = Cl^-$, $Br^-$ or $I^-$) showing the behaviour of the silver electrode at pH ∼ 4, 8 and 12 are depicted in Figs. 1a, 1b and 1c. The first curve is also obtained in more acid solutions (pH ∼ 1.2). It can be seen that in chloride solutions the potential varies appreciably and rather regularly with pCl, up to a certain value which decreases with increase of pH. The potential then shifts towards the values obtained at the same pH values in the absence of chloride ions, indicating that these ions have only a very slight effect in sufficiently dilute solutions. The mode of variation of $E_H$ with pCl along the lower range may be ascribed to the

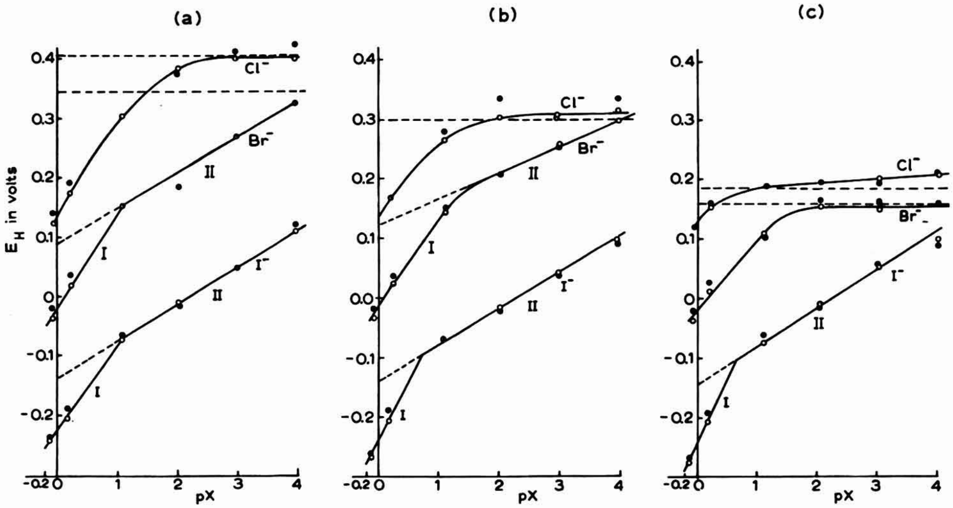

Fig. 1. Silver electrode in halide media at different pH values (●, overnight values).

| | *a* | *b* | *c* |
|---|---|---|---|
| $Cl^-$ | 3.98 | 7.82 | 12.32 |
| $Br^-$ | 4.01 | 7.95 | 11.91 |
| $I^-$ | 4.08 | 8.10 | 12.02 |

existence of a compound type of a silver–silver chloride electrode. This may be tentatively represented by the $Ag|AgCl|Cl_{ad}^-$ system. Chloride ions are preferentially adsorbed on the metal surface, presumably after a thin AgCl film is formed.

The electrode behaves differently in bromide and iodide solutions. In the pH range ~ 4–8, the potential varies linearly with pBr or pI (lines II, Fig. 1) within a certain range (usually > pI 1); the reversible silver–silver halide electrode behaves similarly. In more concentrated solutions, the potential usually shifts towards more negative values than would be expected for a simple rectilinear relationship. This indicates that a layer of AgBr or AgI, is readily established on the metal surface. In the presence of excess halide ions, complex ions of the type $AgX_2^-$ or $AgX_3^{2-}$ may form with subsequent depletion of $Ag^+$ ions in the vicinity of the electrode surface, thus shifting the potential towards more negative values. In more alkaline solutions (pH ~ 12), the behaviour of the electrode in bromide solutions is different from that in iodide solutions. Thus in bromide solution the potentials obtained at pBr ~ 2–4 are much closer to a $Ag-Ag_2O$ than to a $Ag-AgBr$ couple. In iodide solutions, on the other hand, the $Ag-AgI$ potential predominates up to pI 3; the potential recorded at pI 4 deviates to some extent from the straight line relationship.

The behaviour of a silver–silver halide electrode in buffered halide solutions is illustrated by the $E_H-pX$ plots shown in Figs. 2a and 2b. The former curve represents the potentials obtained in solutions buffered within the pH range ~1.2–8. The behaviour of the AgCl and AgBr electrodes in that pH range shows that change of potential is almost directly proportional to variation of p(Cl, Br) up to p$X$ ~ 4. In iodide solutions, however, the linear relationship is only exhibited at pI > 0.3; at

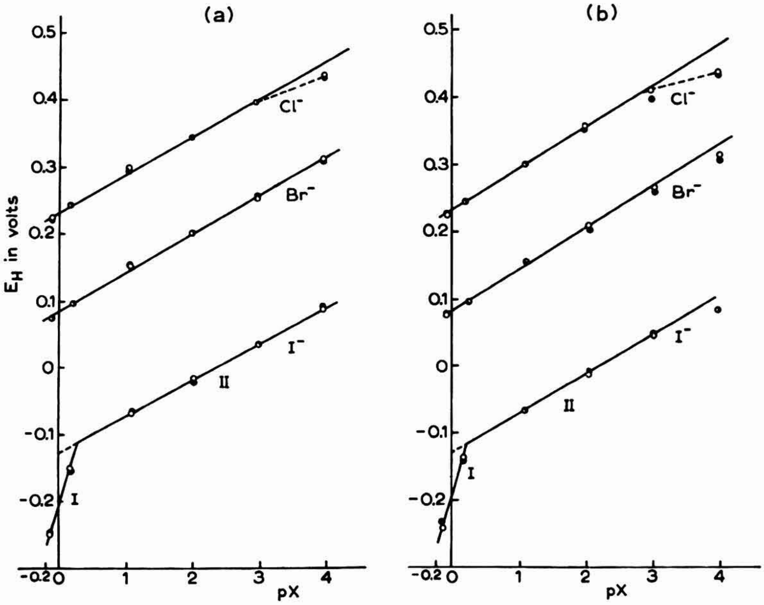

Fig. 2. Silver–silver halide electrode in halide media at different pH values (●, overnight values).

| | *a* | *b* |
|---|---|---|
| $Cl^-$ | 7.82 | 12.32 |
| $Br^-$ | 7.95 | 11.91 |
| $I^-$ | 8.10 | 12.02 |

lower pI values the potentials are too negative, probably because of complex formation.

With all types of Ag–AgX electrode the potentials obtained in alkaline solutions (pH ~ 12) deviate on extreme dilution (p$X$ 4) from the reversible straight line relationship, as with the silver electrode. A probable explanation may be that there is a levelling down of p$X$ due to precipitation of silver hydroxide according to reactions of the type

$$AgX + OH^- \rightleftharpoons AgOH + X^-$$

which proceed in the forward direction in presence of a relative preponderance of $OH^-$ ions.

The electrode potential of Spec-pure silver has also been measured in two series, A and B, of halide- and phosphate-free buffer solutions. Series A includes partially neutralised sulphuric acid of pH 1.12–2.07, Walpole acetic acid–sodium acetate buffers (pH 3.51–5.85), and glycine–sodium hydroxide solutions prepared according to SÖRENSEN AND WALBUM (pH 8.30–12.72). Series B includes phthalate–sodium hydroxide buffers (pH 3.83–5.91), and boric acid–sodium hydroxide solutions (pH 7.79–10.08), all from the Clark and Lubs series.

The electrode potential behaviour as determined by specific anion effects, may be visualised from the $E_H$–pH plots shown in Figs. 3a and 3b. The potentials at pH

1.12 and 2.07 reveal limited metallic dissolution initiated by sulphate anions, becoming more effective at the lower pH value. Acetate anions seem to enhance the corrosion of the metal surface to an extent which decreases with increase of pH, a behaviour which is parallel to the change of solubility of silver acetate. The behaviour in glycine–sodium hydroxide buffers may be ascribed to the deposition of an insoluble layer either of basic acetate in slightly alkaline solutions, or of silver hydroxide in strongly alkaline solution (pH 10.9–12.7).

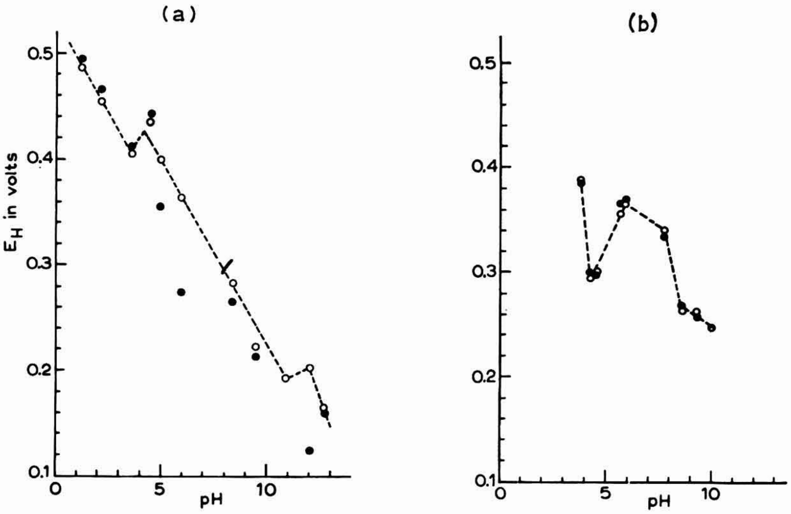

Fig. 3. Silver electrode in buffer solutions (●, overnight values): (a), series A; (b), series B.

The electrode behaviour in solutions of series B may also be correlated to specific anion effects. The behaviour at pH 3.83–4.62 may be explained by the formation of a silver acid phthalate layer on the metal surface, the solubility of which decreases appreciably with increase of pH. At pH 5.74–5.91 normal phthalate may be precipitated at a more or less constant potential. An insoluble silver borate ($AgBO_2$) layer may be also formed in alkaline buffers of pH 7.79–10.08; its solubility decreases with increase of pH.

*Chemistry Department,*
*Faculty of Science,*
*Cairo University (Egypt)*

E. M. Khairy
Mrs. Afaf El-Said Mahgoub

Received August 31st, 1964

# The significance of measurements by the triangular voltage sweep method applied to adsorption reactions

In recent publications[1-5], the triangular voltage scanning method, with potentiostatic control, has been extensively used to study the behaviour of intermediates formed in anodic reactions and, indirectly, the kinetics of these reactions. The method was originally developed by SEVČIK[6] for diffusion-controlled reactions, and early applications were made by DELAHAY AND PERKINS[7] and by LOVELAND AND ELVING[8] who examined the double-layer capacitance at the mercury electrode. Most of the recent work, however, has been applied to activation-controlled reactions involving the chemical and/or electrochemical formation or desorption of intermediates. The interpretation of results obtained for such processes by the potential sweep method has not previously been discussed from a kinetic viewpoint, and the deductions from results obtained for irreversible reactions often leave much to be desired. For ionisation of chemisorbed hydrogen[1,9], which is a relatively reversible process, the interpretation of results is least complicated.

The method is based on a controlled change of the intensive variable, potential ($V$), usually at a constant rate $m = \mathrm{d}V/\mathrm{d}t$ in a multiple[1,2] or single sweep[3] technique. The method, applied to electrochemical desorption, is thus the electrochemical analogue of the flash desorption method for the study of differential desorption and heterogeneity in gas-solid adsorption processes, where temperature is the intensive variable which is changed.

## *Non-steady state kinetic theory of the sweep method*

For an activation-controlled process examined by the voltage sweep method, three contributions to the time-dependent current which passes arise as follows: (i) a non-Faradaic current, $C_{\mathrm{d.l.}}\,\mathrm{d}V/\mathrm{d}t$, associated with charging or discharging the ionic double-layer capacitance, (ii) a pseudo-Faradaic current*, $C\,\mathrm{d}V/\mathrm{d}t$, associated with change of extent of coverage by adsorbed intermediates formed or removed in an electrochemical step; and (iii) kinetic currents, $i_F$, associated with any net reactions which can occur over the range of potentials in which the voltage scan is made to occur. Usually kinetic currents considered in (iii) will be dependent on the behaviour of the intermediates considered in (ii), *e.g.*, with regard to (a) the rate at which such intermediates can be adsorbed or desorbed, and (b) their relative surface coverage. The net current $i_t$ as a function of time in a sweep is thus

$$i_t = C_{\mathrm{d.l.}}\frac{\mathrm{d}V}{\mathrm{d}t} + C\frac{\mathrm{d}V}{\mathrm{d}t} + i_F(t) \qquad (1)$$

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* The term "pseudo-Faradaic" current is used here as it refers to the current associated with charging or discharging the adsorption pseudo-capacitance, $C$, a term previously used[10] to distinguish capacitance effects (associated with potential-dependent coverage by intermediates produced in a Faradaic step in a multi-step overall reaction) from capacitance associated with potential-dependence of adsorbed ionic charge.

where $i_F$ is the current associated with a Faradaic process considered in (iii) and will be dependent on potential and probably time $t$. We shall consider particularly conditions under which $C \gg C_{\mathrm{d.l.}}$, *i.e.*, for ranges of electrode potential in which electrochemical adsorption or desorption of intermediates at appreciable coverages $(0.1 < \theta < 0.9)$ is occurring[10].

It is important to note that $C$ will generally be extensively dependent on potential[10,11] and can also vary with the rate at which the coverage by intermediates associated with $C$ is changed, *i.e.*, with the time-dependent pseudo-Faradaic current. This effect arises because the production or removal of intermediates is usually itself an activation-controlled process exponentially dependent on potential (see below).

The change of coverage $\Delta\theta_t$ caused by passage of the time-dependent charging current $i_t$ will be

$$k'\Delta\theta_t = \int_{t_1}^{t_2} i_t \mathrm{d}t \tag{2}$$

where $t_1$ and $t_2$ are times corresponding to potentials $V_1$ and $V_2$ attained in a (single) sweep, and $k'$, is a proportionality factor relating coverage to charge passed. If the intermediate, the coverage by which is $\theta_t$, is produced in a (anodic) discharge step $I$

$$i_t = k_1(1 - \theta_t) \exp[\beta VF/RT] - k_{-1}\theta_t \exp[-(1 - \beta)VF/RT] \tag{3}$$

where $k_1$ and $k_{-1}$ are terms involving rate constants, reactant concentration in solution, and any double-layer terms which need not be considered further here. The current $i_t$ will be the total net current if the potential is below that at which $i_F$ is significant. This is often the case in charging and discharging processes (*e.g.*, in electrochemical adsorption and desorption of oxygen and hydrogen).

Then

$$\theta_t = \frac{k_1 \exp[V/b] - i_t}{k_1 \exp[V/b] + k_{-1}[\exp - V/b]} \tag{4}$$

where we have taken for brevity $\beta = 0.5$ and written $b = RT/\beta F = RT/(1 - \beta)F$. Equation (4) can be written

$$\theta_t = \frac{k_1 \exp[V/b]}{k_1 \exp[V/b] + k_{-1} \exp[-V/b]} - \frac{i_t}{k_1 \exp[V/b] + k_{-1}[\exp - V/b]} \tag{5}$$

In the galvanostatic case $i_t$ is made constant and the potential follows the coverage attained. However, in the sweep method the current is time-dependent. In eqn. (5), it is seen that the first term on the r.h.s. is the coverage attained at potential $V$ at zero net charging rate (*i.e.*, under quasi-equilibrium) and the second term gives the effect of the driving current on $\theta_{t,V}$.

We can then obtain the adsorption pseudo-capacitance $C_V$[10] associated with the potential dependence of $\theta_t$ as

$$\frac{1}{k'}C_V = \frac{\mathrm{d}\theta}{\mathrm{d}V} = \frac{f(V)\dfrac{k_1 \exp[V/b]}{b} - \dfrac{k_1 \exp[V/b]}{b}(k_1 \exp[V/b] - k_{-1}\exp[-V/b])}{[f(V)]^2}$$

$$- \frac{f(V)\dfrac{\mathrm{d}i_t}{\mathrm{d}V} - \dfrac{i_t}{b}(k_1 \exp[V/b] - k_{-1}\exp[-V/b])}{[f(V)]^2} \qquad (6)$$

where $f(V)$ is defined as $k_1 \exp[V/b] + k_{-1}\exp[-V/b]$. The first term is obviously[10,12] proportional to the equilibrium pseudo-capacitance, $C_{E,V}$, given by

$$\frac{C_{E,V}}{k'} = \frac{2k_1 k_{-1}}{b[f(V)]^2} \qquad (7)$$

Noting that

$$i_t = C_V\frac{\mathrm{d}V}{\mathrm{d}t} \quad \text{and} \quad \frac{\mathrm{d}i_t}{\mathrm{d}V} = \mathrm{d}\left(C_V\frac{\mathrm{d}V}{\mathrm{d}t}\right)\Big/\mathrm{d}V = \frac{\mathrm{d}V}{\mathrm{d}t}\cdot\frac{\mathrm{d}C_V}{\mathrm{d}V}, \qquad (8)$$

since $\mathrm{d}V/\mathrm{d}t$ is independent of $V$ for a single sweep, then

$$\frac{1}{k'}C_V = \frac{\mathrm{d}V}{\mathrm{d}t}\left(\frac{f(V)\left(\dfrac{C_V}{b} - \dfrac{\mathrm{d}C_V}{\mathrm{d}V}\right) - \dfrac{2k_{-1}\exp[-V/b]}{b}\cdot C_V}{[f(V)]^2}\right) + \frac{C_{E,V}}{k'} \qquad (9)$$

When $\mathrm{d}V/\mathrm{d}t \to 0, C_V \to C_{E,V} \neq 0$ and $\mathrm{d}C_V/\mathrm{d}t = (\mathrm{d}C_V/\mathrm{d}V)(\mathrm{d}V/\mathrm{d}t) \to 0$, so that relation (9) has the correct form since it must give the equilibrium capacitance $C_{E,V}$ at zero sweep rate when the time-dependent charging current is zero.

It is clear that the result (9) implies a complex variation of $C_V$ with sweep rate involving several terms in $\mathrm{d}V/\mathrm{d}t$ (since $\mathrm{d}C_V/\mathrm{d}t$ involves $\mathrm{d}V/\mathrm{d}t$) and interpretation of $C_V$ measured at appreciable sweep rates will not be a simple matter. Similarly, the extrapolation of $C_V$ to $C_{E,V}$ will not be easily achieved. At low sweep rates, however, a linear extrapolation might be an acceptable approximation from eqn. (9).

Generally it is also seen that the method can give no simple result for evaluation of terms which are in $f(V)$. The steady slow point-by-point potentiostatic examination of a current potential relationship is to be preferred for evaluating kinetic behaviour, and the direct and differential galvanostatic method[13,14] is to be preferred for dealing quantitatively with charging processes since $i_t$ is kept constant and is measured, and the resulting equations for $\theta_t$ and $C_V$ are much simpler[14]. $C_V$ can also be obtained as a simple function of charging current $i$ as[14]:

$$\frac{C_V}{k'} = \frac{C_{E,V}}{k'} - \frac{i(k_{-1}\exp[-V/b] - k_1[\exp V/b])}{[f(V)]^2} \qquad (10)$$

The charge $q_t$ associated with the change of coverage $\Delta\theta_t$ between two potentials will also be a function of $\mathrm{d}V/\mathrm{d}t$ in multiple sweep experiments (but not necessarily in a single sweep [ramp] between two potentials)*. Thus if $\mathrm{d}V/\mathrm{d}t$ is sufficiently large (*cf.*, the a.c. case at high frequency), it seems that there must be a dispersion of the value of $\theta$ corresponding to $q$ at a given potential, since the charging process producing and removing the adsorbed species cannot keep up with the rate of change of $V$, if

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* This arises since steady-state conditions can be established at each end of an ascending or descending ramp signal.

the charging process has other than an "infinite" degree of reversibility. The use of the multiple sweep method for estimating coverage by intermediates in complex reactions by integrating the $i_t$–$t$ relation must therefore be questioned except for relatively reversible reactions such as hydrogen deposition and ionisation at catalytic metals.

Also, there will tend to be indirect effects of sweep rate on *kinetic* (Faradaic) currents. Usually the latter are determined in part by coverage by intermediates involved in the reaction itself or by coverage by species *e.g.*, oxides produced in competing reactions (*e.g.*, in anodic oxidations in aqueous media). The coverage at a given potential will depend on $dV/dt$, so that the kinetic currents can also be dependent on $dV/dt$, and may be difficult to distinguish from pseudo-Faradaic currents arising only from potential dependence of coverage.

In complex anodic reactions it seems, therefore, that the method must be applied with caution and that only qualitative or semi-quantitative kinetic and coverage information can be derived. Further details and applications of these calculations will be published elsewhere[14].

*Acknowledgement*

Grateful acknowledgement is made to the Defence Research Board and the General Motors Company for support of work on anodic oxidations, the interpretation of which has led to the above theoretical work. Discussion with E. Gileadi (*cf.* ref. 14) is also acknowledged.

*Department of Chemistry,* B. E. Conway
*University of Ottawa (Canada)*

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Received August 25th, 1964

# Book Reviews

*Les Liquides Simples*, by ARNOLD MÜNSTER, Gauthier-Villars et Cie, Paris, 1964, 77 pages, 14 F.

This monograph is the outcome of a series of lectures given by Professor MÜNSTER at the Faculté de Sciences de Paris. The first chapter contains a general introduction and a discussion of the Lennard-Jones and Devonshire cell model; the second, a discussion of the various attempts to improve this model; the third discusses the radial distribution function and Monte Carlo calculations, and the fourth is concerned with the theorem of corresponding states and its application to liquid mixtures. The intention of the author was to present an up-to-date account of the theory of the liquid state, emphasizing the basic ideas and the comparison with experiment, and avoiding mathematical detail. In this he has succeeded quite admirably. This book provides an excellent introduction to a difficult and extensive subject for anyone with a basic grounding in elementary statistical mechanics. It can be thoroughly recommended.

Certain of the numerical results quoted in Tables 3–5 are reduced quantities, and this is not indicated in the table headings.

A. J. LEADBETTER, Chemistry Department, University of Bristol

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*New Sources of Energy*, Vol. 1, *General Sessions*; United Nations, N.Y., 1963, ix + 218 pages, $2.50

This is part of the proceedings of the United Nations Conference held in Rome in August 1961. There are two parts, the general session surveying the potentialities of new sources of power for under-developed countries, and a technical session concerned mainly with problems of energy storage. The new sources considered are solar energy, wind power and geothermal energy, so that the electrochemist will find most of the material of direct interest to him in the technical session where electrochemical storage methods are discussed. After a general survey by F. DANIELS, F. T. BACON assesses the economic possibility of storage using an electrolyser combined with a hydrogen–oxygen fuel cell. G. E. EVANS presents a detailed comparison of this type of system with the lead acid accumulator. The storage of solar energy, in particular, by using thermally regenerative fuel cells is considered by C. R. McCULLY, who surveys a variety of possible systems, and by R. C. WERNER and T. A. CIARLARIELLO who emphasise the advantages of the LiH system. R. J. MARCUS and H. C. WOHLERS present the results of experiments on the photochemical decomposition of water and of NOCl; the latter is the more promising but no fuel cell is yet available for releasing the stored energy.

It is to be hoped that representatives from the under-developed countries took a larger part in this conference than is apparent from this volume; this vital subject is one where detailed co-operation is essential between those with advanced technological knowledge and those with knowledge of local requirements and conditions.

ROGER PARSONS, Chemistry Department, University of Bristol

*Electroanalytical Abstracts*, edited by G. MILAZZO, Birkhäuser Verlag, Basel, bimonthly, 150 SF per annum.

In the dissemination of knowledge, abstracting journals play an important role at the present pace of scientific publishing. It is still difficult to decide how far the specialization of abstracting journals should be pursued — whether it is preferable to have one abstracting journal for chemistry (instead of the existing three) or one for each specialization (*e.g.*, electrochemistry, reaction kinetics, heterocyclic chemistry etc.). It is also questionable how far the efforts made by the more general abstracting journal should be duplicated in the more specialized. It is doubtful whether the conditions (high price and great space requirements) that at present make a journal like Chemical Abstracts inaccessible to private subscribers will change in future. The present division of Chemical Abstracts into sections is unfortunate for electrochemists, who can find their abstracts in all existing sections. A similar situation exists also for other chemists interested more in methods than in subjects. A most useful approach would be the publication of a great number of highly specialized sections by reprinting from the general abstracting journal *all* abstracts concerned with a given specialization. The economic difficulties involved are evident. Hence, at present and in the near future the help offered by a specialized abstracting journal such as Electroanalytical Abstracts is to be welcomed. The journal should offer abstracts, rather descriptive than informative, as fast as possible for a price accessible even for a private purse. These conditions are either fulfilled or approached in the Journal under review; but the specialized journal should also cover the field at least as completely as the Chemical Abstracts. The present reviewer doubts whether at the planned rate of approximately 2000 abstracts yearly it is possible to fulfil this aim even to a considerable fraction, not to speak about 100%. In his 1964 review in Analytical Chemistry, WAWZONEK recorded, in the two-year period 1962–63, over 1100 papers concerning organic polarography alone. Hence for a good coverage of fundamental electrochemistry, apparatus, polarography, amperometry, potentiometry, conductometry, electrolysis, coulometry, electrophoresis and other methods (which are abstracted in Electroanalytical Abstracts) the present reviewer would guess that 4000–5000 abstracts yearly would be necessary.

Nevertheless, even at the present extent, Electroanalytical Abstracts are helpful to an electrochemist, although they may not release him from the duty to follow carefully one of the general abstracting journals. The level of the abstracts remains about the same as in the predecessor of this Journal, the "Abstract Section" of the Journal of Electroanalytical Chemistry, which even the graphical arrangement resembles. In the two issues reviewed, however, some abstracts seem to be too concise, but this is perhaps due to the transition period where the gap between the "Abstract Section" and the new Journal was to be covered. Departures from conventional symbols and terminology are however regrettable. The present reviewer doubts whether any polarographer when consulting the section devoted to polarography, will be familiar with symbols like $V_{\frac{1}{2}}$ (instead of the normal $E_{\frac{1}{2}}$) and terms like half-wave tension (instead of half-wave potential). Such innovations should be used first in the original papers of those who try to promote them and only when accepted by the greater part of the chemical community should they be introduced to an abstracting journal.

P. ZUMAN, Polarographic Institute, Prague

*Advances in Analytical Chemistry and Instrumentation*, edited by C. N. REILLEY, Vol. 2, John Wiley and Sons, London and New York, 1963, 408 pages, 115 s.

The editor of this series (Vol. 1 was reviewed 4 (1962) 62) offers "a reasonably complete review of recent developments ... a dry and terse cataloguing of the literature without description or evaluation is avoided" and this objective is achieved by the various authors. Unfortunately the six topics under review are a heterogeneous collection which puts the book into the category of a source book for references to the original literature for new techniques. Consequently it is likely to find its way onto library shelves rather than into private collections.

Progress in qualitative organic chemical analysis is systematically reviewed by F. FEIGL, R. BELCHER and W. I. STEPHEN. It is surprising to find that this Anglo–South American enterprise covers the literature only up until 1958 — a lapse of five years prior to publication. Much in this field of study tends to be dull and limited in approach and supplies an enormous number of facts about trivial matters. Surely, spectroscopy in its various forms is the modern approach to the subject.

G. MATTOCK (Electronic Instruments Limited) commences his contribution on *Laboratory pH Measurements* with the statement that pH measurements are deceptively easy and then proceeds in excellent style to indicate where the limitations and deceptions lie. His article is essentially a modern introduction for the novice rather than a report on current developments for the specialist. One unfortunate misprint should be noted: on page 44, at the top of column 4 in Table 1, "phosphate" should read "phthalate".

W. KEMULA and Z. KUBLIK (Polish Academy of Science, Warsaw) discuss the hanging mercury drop electrode which they have done so much to popularise as a useful analytical tool. They also include brief remarks on related static mercury electrodes. Most of their clear and helpful article is concerned with voltage sweep chronoamperometry and with stripping methods.

*The Mass Spectra of Organic Molecules* is clearly and critically presented by S. MEYERSON and J. D. MCCOLLUM (American Oil Company). After introducing the chemical basis of mass spectra, they illustrate the interpretation by features shown by carbonyl compounds and allylic and related ethers, with special emphasis upon rearrangement–dissociation processes since these are the most serious complications in interpretation.

The article by P. ZUMAN (Polarographic Institute, Prague) deals, like the one on pH, with an established technique. Dr. ZUMAN discusses the information available from classical polarography with the ease and clarity that we expect from him. The discussion of indirect methods for the determination of organic materials which are not electro-active is particularly useful. He includes two main classes: compounds which may be made electro-active by previous chemical reaction and compounds which react with some other species which is electro-active to form an inactive product.

The last article, on *Reaction Rate Methods* by H. B. MARK, L. J. PAPA and C. N. REILLEY, might well be considered the most important; it occupies a third of the book and it deals with a subject not often considered as a branch of analytical chemistry. The main theme, developed in sections III, IV and V, is the analysis of a mixture by studying the kinetics of reaction of the components which react at different rates. A variety of mathematical techniques is discussed with emphasis on the accuracy which may be expected. This is essentially an extension of the techniques used in the classical study of chemical kinetics. The solution of these problems, using an analogue computer, is discussed briefly in section IX; so briefly in fact that a reader ignorant of the properties of an operational amplifier would at best be stimulated to read some of the references quoted. Examples of the application of differential rate analysis are given in section VI, preceded by a sixteen-page summary of the theory of organic reaction mechanisms and followed by thirty-eight tables of relative reaction rates of organic compounds intended to suggest possible applications of the method. The discussion of catalysed and induced reactions includes a section on catalysed electrode reactions. This seems a little beyond the scope of the article, although useful analogies with electrode processes are drawn at several points elsewhere. The article begins with a section on methods for studying fast reactions (continuous flow, relaxation methods, etc.) including a generalised theoretical discussion. Since all the methods discussed as practical examples are of the classical type, it seems to be a mistake to have put this part first. Presumably the object is to stimulate extensions of the method to faster reactions and this illustrates the best feature of the article — that it is enthusiastically oriented towards the future rather than towards the past.

LESLIE HOUGH and ROGER PARSONS, Department of Chemistry, University of Bristol

*J. Electroanal. Chem.*, 8 (1964) 492–493

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*Determination of pH, Theory and Practice*, by ROGER G. BATES, John Wiley & Sons Inc., New York, London and Sydney, 1964, 435 pages, £5.0.0.

pH Measurements are such a recurring feature of the chemical scene that even the most humble adherent of chemistry can become tempted to speak of pH with the confident fluency of a savant. Let's face it: remarkably few of us who so diligently record millions of pH values every year really know what exactly is being measured when we observe the meter reading. Fortunately, in a good many instances such ignorance doesn't matter, but if one sets out to comprehend the meaning of a pH meter reading, then the task will be found to abound in conceptual niceties and unwelcome qualifications. Even if simplicity here is elusive, an authoritative text to consult is not, and pH users could hardly do better than have near to hand a copy of Dr. R. G. BATES' revised edition of his 1954 book on this subject.

The new book is about one-third longer than the old, but retains the same structure in that, broadly, the early parts describe theory and principle while the later parts deal with technique and equipment. Chemists familiar with the field will appreciate the enormous difficulty of achieving a blend and a balance among the diverse intricacies of "pH", but the author has done this superbly without making the result unpalatable, as would almost inevitably have happened in less masterly hands. The essence of Dr. BATES' treatment is that it is sensible. On the one hand he describes in restrained detail the complications of connecting what can be observed with what can be defined; but he does not overlook the fact that countless measurements on countless pH meters are made without recourse to their meaning in terms of individual ionic activities and without purposefully accounting for such factors as liquid junction potential, temperature equilibrium, and meter calibration. The instrumental steadiness and numerical discrimination of modern pH meters are a deceptive invitation to some attractive interpretation solely in ionic language, but the author is at pains to explain the pitfalls awaiting the unwary.

A valuable addition made by the author has been a chapter on colorimetric pH measurements and it was this extension of scope which impelled a change of name when the 1954 book came to be revised. There is also some discussion of glass electrodes sensitive to other than hydrogen ions, so that the measurement of pNa is put in the same context as the alkaline error of the glass electrode. A comparable approach could have been made to the estimation of pOH (a more realistic parameter than pH for alkaline solutions), but perhaps to introduce this aspect may be regarded as premature. At least, the inclusion of a section on pOH would have brought out a revealing contrast between the effects of temperature on pH and pOH viewed as working measures of acidity and alkalinity. In this connection pH "measurements" near 100° are already a practical reality, but it seems mistaken to rely on this facility if the numerical observations (whatever they may measure) are judged on the familiar pH scale applying only to 25°. The neutral point moves considerably with temperature, and pH 7.0 is (in practical parlance) acid at 0°, neutral at 25°, and alkaline at 100°. Dr. BATES could have rubbed off the strangeness of these facts for many pH users.

As a reference book the new volume is a paragon. The type is bold and clear, the paper is suitably opaque, and the binding is flexible. The left-hand pages are headed with the chapter title and the opposite pages carry the section heading. The text is free from typographical error, and the indexes are excellent. References appear at the foot of the page and are up-to-date. Useful footnotes and comment are interspersed with these references, so that the small type sometimes spills over to the next page — a tolerable irritation. The prose is impeccable and the style detached, with occasional reassuring excursions to the personal. The subject matter is presented succinctly and convincingly, but perhaps the best demonstration of the author's fitness for his task is the absence of his name from the author index. Its inclusion would have been superfluous!

E. C. POTTER, Central Electricity Research Laboratories, Leatherhead

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# MECHANISMS OF SOLID FRICTION

edited by P. J. BRYANT and M. LAVIK, Midwest Research Institute, Kansas, Missouri, and G. SALOMON, Central Laboratory T.N.O., Delft

A conference was held on the Fundamental Mechanisms of Solid Friction at the Midwest Research Institute during September 1963. Its objective was to provide for formal presentations of current research and to encourage informal discussions among the active scientists in the field. The conference dealt with the topics of surface energy and temperature considerations, ionic solids, lamellar solids, metallic friction and metallic wear. The full proceedings were published as the first two issues of the journal WEAR, volume 7, 1964. It was suggested that a bound volume of the Proceedings would be welcomed, and the publishers hope that this compact volume will be a useful guide for workers in the growing field of wear, friction and lubrication research.

viii + 224 pages, 38 tables, 128 illustrations, 278 lit. references, 1964, 50s.

# ADHESION AND COHESION

edited by Philip WEISS, Head, Polymers Department, Research Laboratories, General Motors Corporation, Warren, Michigan

This volume on "Adhesion and Cohesion" contains the proceedings of the fifth of a series of annual symposia sponsored by the General Motors Research Laboratories. The purpose of this symposium was to discuss and interpret fundamental knowledge and to interrelate it with the complex phenomena of adhesion and cohesion.
This exchange of ideas made it clear that an adequate theory must include many concepts, e.g. intermolecular forces, imperfections, stress concentrations, surface topography, wetting, and chemical constitution.
The papers presented at the symposium, as well as the informal discussions, are included in this book and the sequence is that of the symposium program.

viii + 272 pages, 47 tables, 121 illustrations, 292 lit. references, 1962, 60s.

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