

simultaneous hydrogen evolution. Addition of boric acid makes it smaller as the hydrogen evolution associated with nickel deposition is largely avoided.

CONCLUSIONS

An anodic peak obtained for the oxidation of codeposited hydrogen, makes it possible to assess the extent of hydrogen evolution occurring in the process of nickel deposition. Progressive diminution in its size, brought about by the additions of boric acid, indicates that boric acid inhibits hydrogen evolution.

Cyclic voltammetry, in recent years, has led to the development of a rapid and novel method, in the monitoring of electrolytes. The present study provides similar scopes for nickel electrolytes employed in the plating as well as electrowinning processes. It would be possible to estimate the impurities and other constituents present in the electrolyte by generating cyclic voltammograms and analysing their features.

REFERENCES

1. J.P.Hoare, *Electrochim. Acta* 27, 1751 (1982)
2. J.P.Hoare, *J. Electrochem. Soc.* 133, 2491 (1986)
3. J.P.Fast *Interaction of Metals and Gases*, P.92. Barnes and Noble Inc., New York (1972)
4. L.B.Harris, *J. Electrochem. Soc.* 120, 1034 (1973)
5. I.Epelboin and R.Wiart, *J. Electrochem. Soc.* 118, 1577 (1971)
6. B.V.Tilak, A.S.Gendron and M.A.Mosoiu, *J. Appl. Electrochem.* 7, 495 (1977)

(Received, 29 Juni 1993
Revised form, 2 November 1993)

THE ELECTROPHORETIC EFFECT IN ELECTROLYTE SOLUTIONS

Victor M.M. Lobo and Ana C.F. Ribeiro
Department of Chemistry, University of Coimbra
3000 Coimbra - Portugal

Abstract

The concept of the electrophoretic effect in electrolyte solutions and the way it has been presented in the literature is critically discussed.

Key words: solutions, electrolytes, electrophoretic effect.

The interpretation of thermodynamic and transport properties of electrolyte solutions leads to models concerning the structure of those solutions and concepts about the hydrodynamic behaviour of ions moving through their media. One of those concepts is called *electrophoretic effect*. However, it has been presented in the literature in a variety of different ways, sometimes not equally clear.

The term electrophoretic effect firstly appears in the literature in 1932 [1] as follows:

"There are two different effects to be considered, namely the direct transfer of electric forces between the ions and a hydrodynamic effect, the so-called electrophoresis. The later effect was recognized by Debye and Huckel, while the former had been expected for a long time by those familiar with the properties of electrolytes.

The *electrophoresis* is most simply described and estimated for the case of electrical conduction where, for an electric field E ,

$$k_0 = 0; k_i = e_i E \quad (i = I, \dots, s)$$

The atmosphere of an ion of charge e_j will contain the total electric charge $-e_j$ and consequently be subject to a total force $-Ec_j$ in the field E . This force will be taken up by the liquid in which the ions of the atmosphere are embedded, and cause hydrodynamic motion in the direction of the force $-Ec_j$. For an estimate of the effect, we may assume the entire charge $-e_j$ of the atmosphere situated at a distance equal to the mean radius $1/k$, uniformly distributed on a spherical shell. Then according to Stoke's law, the interior of the sphere will move with the velocity

$$\Delta v_j = -Ee_j / 6\pi\eta k^{-1} = -Ee_j k / 6\pi\eta \quad (4.1.6)$$

where η = viscosity. The liquid that immediately surrounds the central ion will be moving with the velocity Δv_j , and this ion, as it migrates in the electric field, must swim in a countercurrent of the magnitude (4.1.6). If the ion had no atmosphere, it would move with the velocity

$$k_j / \rho_j = Ee_j / \rho_j$$

Surrounded by an atmosphere, the ion is subject to a force $k_j - \Delta k_j$; but the velocity corresponding to this force, namely

$$(k_j - \Delta k_j) / \rho_j$$

describes the motion relative to a neighborhood moving with the velocity Δv_j , so that the net velocity will be

$$v_j = \Delta v_j + (k_j - \Delta k_j) / \rho_j$$

or in the particular case of electric conduction

$$v_j = \frac{Ee_j - \Delta k}{\rho_j} - \frac{Ee_j k}{6\pi\eta} \quad ."$$

Since then, prominent researchers in the field of electrolyte solutions have referred to the effect as may be seen in the following citations, given by chronological order:

Harned 1947 [2]

"When an electrolyte diffuses into a solvent, both ions travel with the same velocity, a phenomenon required by electrical neutrality. In this case, electrophoresis occurs because as the ions move in one direction, they take positions previously occupied by the water molecules which in a system at constant volume must move in the opposite direction. The calculation of the electrophoretic

effect will require therefore an estimate of the volume force acting on the water molecules". . . . "Consequently, this estimate of the electrophoretic effect can only be expected to approach validity at low concentrations of electrolytes. Deviations due to ion-solvent and other short-range ionic interactions may be expected at higher concentrations and at the present time there exists no means of computing their magnitudes".

Stokes 1953 [3]

"The theory developed by Onsager and Fuoss results in an expression for the diffusion coefficient D of a dilute electrolyte solution, which may conveniently be written as

$$D = (1 + c d \ln y_{\pm}/dc) (D^0 + \Delta_1 + \Delta_2)$$

Here Δ_1 and Δ_2 are small concentration dependent corrections to the Nernst limiting value D^0 , and originate in the electrophoretic effect, i.e., the transfer of velocity from one ion to another via the solvent. On working through the theory as presented in references (1), one finds that Δ_1 and Δ_2 arise, respectively, from the first and second terms of the expansion of an exponential function..."

Adamson 1954 [4]

"Since there is no net motion of the system, the volume forces on the ions and on the solvent must cancel on the average, but due to the ion atmosphere there is a local force excess in the vicinity of each ion. Onsager and Fuoss considered that the force excess arising in a given spherical shell imparts a velocity increment to the medium as though the shell were a Stoke's law sphere. The correction to the diffusional velocity which results is known as the electrophoretic effect. Longworth strongly supported this treatment although it has been questioned by Van Rysselberghe and, recently, Harned has commented that the theory may be either wrong or incomplete for the higher valence type electrolytes".

Harned and Owen 1957 [5]

"... the theory of the diffusion of a single electrolyte in dilute solutions has been developed in detail. In this case, electrical neutrality requires that both positive and negative ions move with the same velocity. Under these conditions the ionic atmospheres suffer no deformation and the time of relaxation effect vanishes. Further, since the electrolyte moves in one direction and the solvent by replacing it moves in the opposite direction, an 'electrophoretic' effect exists".

Robinson and Stokes 1959 [6]

There are two main effects of the interaction between the electric charge of the ions: these are the electrophoretic effect and the relaxation effect. The electrophoretic effect arises in the following way. When an ion moves through a viscous medium it tends to drag along with it the solution in its vicinity. Neighbouring ions therefore have to move not in a stationary medium but with or against the stream according as they are moving in the same direction as the first ion or oppositely. The effect will clearly be concentration-dependent, falling to zero at infinite dilution, and its computation will require the use of the distribution function, since it involves the distances between ions".

Moore 1963 [7]

"A second electrical action that lowers the mobility of the ions is called the electrophoretic effect. The ions comprising the atmosphere around a given central ion are themselves moving, on the average in the opposite direction, under the influence of the applied field. Since they are solvated, they tend to carry along with them their associated solvent molecules, so that there is a net flow of solvent in a direction opposite to the motion of any given (solvated) central ion, which is thus forced to "swim upstream" against this current.

The steady state of motion of an ion can be found by equating the electric driving force to the sum of the frictional, asymmetric, and electrophoretic retardations".

Pikal 1971 [8]

"The electrophoretic effect is a hydrodynamic effect which is due to a local volume force in the liquid surrounding an ion. Thus, a given ion does not move with respect to a medium at rest, but due to the presence of the ion atmosphere, migrates in a medium which is itself in motion. For convenience we shall consider the one-dimensional case. The final result for the diffusion coefficient is equally applicable in three dimensions".

Robbins 1972 [9]

"The *electrophoretic effect*. The migration of an ion through a solution tends to carry along solvent molecules in its wake. Ions travelling in the opposite direction have to move against this solvent flow, a situation referred to as the electrophoretic effect. As the system is diluted, ions and their associated solvent molecules become more widely dispersed, there is less hindrance to the motion of a given ion, and Λ rises as c diminishes".

Tibor Erdey-Gruz 1974 [10]

"The other phenomenon arising from electric interaction of ions is the electrophoretic effect; the fact that the water molecules in the immediate vicinity of ions move with them and other water molecules are also carried along by them is responsible for this phenomenon. Namely, the ions move in a flowing medium that carries them more or less away. Due to the presence of the ion atmosphere, positive ions restrict the movement of negative ions to a greater extent than that of positive ions, while negative ions have a greater effect on the positive ones in their ion atmosphere. If positive and negative ions move in opposite directions, the electrophoretic effect also appears in the increase of frictional resistance and in the decrease in mobility. On the other hand, the co-current movement of ions of opposite charge can give rise to an increased mobility by this effect. (...)

The electrophoretic effect in diffusion also alters the mobilities of ions, but in a different way than in electric conduction. In diffusion, the interaction of the ionic charges slows down the ions of higher mobility, while it accelerates those of lower mobility. Consequently, the electrophoretic effect increases the mobility of ions of lower mobility and has a reversed effect on the faster ones in the given electrolyte. If the mobilities of different ions are identical, the electrophoretic effect disappears".

Bockris 1977 [11]

"The term *electrophoresis* is generally used to describe the migration of particles of colloidal dimensions (10 to 10,000 Å) in an electric field. It is appropriate, therefore, to describe the migration of the ionic cloud as an *electrophoretic effect*.

The interesting point, however, is that, when the ionic cloud moves, it tries to carry along its entire baggage, the ions and the solvent molecules constituting the cloud *plus* the central ion. Thus, not only does the moving central ion attract and try to keep its cloud (the *relaxation effect*), but the moving cloud also attracts and tries to keep its central ion by means of a force which is then termed the *electrophoretic force* F_E ".

Horvath 1985 [12]

"The electrophoretic effect arises from electric interaction ions. As a consequence of the interaction, water molecules are also carried along with the moving ions. The electrophoretic effect influences the mobilities of ions. The interaction of the ionic charges slows down ions of higher mobility, while it accelerates those of

lower mobility. There is no electrophoretic effect on ions of identical mobility (Stokes, 1953).

The diffusion coefficients of ions in infinite dilute solutions can be calculated from the Nernst equation".

Wright 1988 [13]

"We also have to consider the effect of the solvent on the movement of the ion and its ionic atmosphere under an applied field. This is discussed under the heading the electrophoretic effect.

When an ion moves, it carries its ionic atmosphere with it. This ionic atmosphere is made up, in part, of ions which have the same charge as the central ion and will move in the same direction as the central ion under an external field. It also contains ions which will have an opposite charge, and will move in the opposite direction.

If the central reference ion and an ion of opposite sign in the ionic atmosphere are passing each other, solvent will be pulled along with each ion but in opposite directions. So the central reference ion of the pair will, in effect, 'see' solvent streaming past itself in the opposite direction, and this will exert a viscous drag on the central reference ion, slowing it down.

If the central reference ion and an ion of like sign in the ionic atmosphere are passing each other, the differing speeds of the two ions will cause streaming of the solvent past the central reference ion. If the ion on the ionic atmosphere is overtaking the reference ion, the reference ion will be pulled along by the solvent streaming past it in the same direction, resulting in an increase in its velocity. If the central reference ion is overtaking the ion of the ionic atmosphere, it will experience a viscous drag by the solvent around the ionic atmosphere ion which will make this solvent appear as though it were, in effect, moving in the opposite direction to the central ion.

These effects are covered by the general term 'electrophoretic effect', and their net effect is always to slow the ion down, resulting in a lower ionic conductance than would be expected if there were no ionic atmosphere".

In our point of view the concept should clearly show the following ideas: when an ion moves in an electrolyte solution, it drags along its "ionic atmosphere" (or at least part of it, depending on our definition of the ionic atmosphere); the movement of the other ions is consequently affected. This is understood in the Onsager and Fuoss [1] paper, but not so clearly shown in some of the other descriptions above cited.

Of course, it may be said that the above is more of an hydrodynamic effect than an electrophoretic effect.

However from the history of the evolution of the concept, we understand that initially it was termed as electrophoretic effect when studying electric conduction where we actually have an applied external electrical field which creates a situation similar to the previously known phenomenon of electrophoresis (e.g. in paper electrophoresis). In diffusion we do not have an external field, but the fact that ions move with different speeds creates an internal electric field; equations may then be applied to attempt to quantify it. Therefore there has been a tendency to keep the name "electrophoretic effect" for such treatment. Such fact, may justify Horvath's [12] indication that "There is no electrophoretic effect on ions of identical mobility". However, even in such a case, we still have the ions moving along with its "ionic atmosphere" which consequently affect movement of other ions.

References

- [1] - L. Onsager and R.M. Fuoss (Irreversible processes in electrolytes. Diffusion, conductance, and viscous flow in arbitrary mixtures of strong electrolytes), J. Phys. Chem. 36, 2689 (1932).
- [2] - H.S. Harned (The quantitative aspect of diffusion in electrolyte solutions), Chem. Rev. 40, 461 (1947).
- [3] - R.H. Stokes (The electrophoretic corrections to the diffusion coefficient of an electrolyte solution), J. Am. Chem. Soc. 75, 4563 (1953).
- [4] - A.W. Adamson (The diffusion and self-diffusion of electrolytes and hydration effects), J. Phys. Chem. 58, 514 (1954).
- [5] - H.S. Harned and B.B. Owen (The physical chemistry of electrolytic solutions), (1957).
- [6] - R.A. Robinson and R.H. Stokes (Electrolyte solutions), 2nd Ed., Butterworths, London (1959).
- [7] - W.J. Moore (Physical Chemistry) 4th Ed., Lowe and Brydone Ltd, London (1963).
- [8] - M.J. Pikal (Ion-pair formation and the theory of mutual diffusion in a binary electrolyte), J. Phys. Chem. 75, 663 (1971).
- [9] - J. Robbins [Ions in solution (2). An introduction to electrochemisatry], Osgord University Press (1972).
- [10] - T. Erdey-Gruz (Transport phenomena in aqueous solutions), Adam Hilger, London (1974).

- [11] - J. O'M. Bockris and A.K.N. Reddy (Modern electrochemistry. An introduction to an interdisciplinary area), Plenum Press, New York, 6th printing (1977).
- [12] - A.L. Horvath (Handbook of aqueous electrolyte solutions), John Wiley and Sons, New York (1985).
- [13] - M.R. Wright (The nature of electrolyte solutions), MacMillan Education (1988).

(Accepted, 17 January 1994)

ELECTROCHEMISTRY OF SULPHUR IN ALKALI SOLUTIONS

M. JAYALAKSHMI AND V. S. MURALIDHARAN

CENTRAL ELECTROCHEMICAL RESEARCH INSTITUTE
KARAIKUDI-623 006, INDIA

SUMMARY

Voltammetric studies were carried out on gold electrode to identify the oxidation products of elemental sulphur in alkali solutions. The oxidation of HS^- and S_2^{2-} is reversible followed by oxidation to sulphur which gets incorporated in the hydrous films on gold. Pitting occurs when the film break and the pitting susceptibility of gold increased with alkali concentration. On the sulphur covered gold surface, no oxygen reduction was observed and H_2S evolved along with hydrogen.

KEY WORDS: Sulphur electrochemistry, Voltammetry, Gold electrodes

INTRODUCTION

Towards the development of porous iron electrodes for use in Ni-Fe alkaline batteries, an activated iron electrode was developed [1]. The activation of the porous iron electrode was carried out in 6M KOH solutions containing 32gpl elemental sulphur by passing various cathodic currents. The improved performance of these electrodes prompted us to study the oxidation behaviour of sulphur in high alkali solutions. In order to identify the products of oxidation of sulphur, voltammetric studies were carried out on gold which offers an extensive potential range over which there is no interaction of gold with water. A few studies were reported on the Au/S^{2-} and Au/SO_2 interactions in aqueous solutions [2-4]. Place exchange mechanism with the formation of surface oxides [5,6], Au/O^{2-} may lead to similar process on Au/S^{2-} or breakdown of passive oxide film may take place in presence of sulphur. The paper presents the oxidation products of sulphur and their effects on gold surface.