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THE ELECTRIC DOUBLE LAYER: A PHYSICAL REALITY?

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Synopsis Interfacial potential differences can only be interpreted in terms of a physical reality between phases of identical chemical composition. Many substances acquire a charge when immersed in water and migrate under an applied electric field. This is usually interpreted in terms of an ionic double layer at the surface and the zeta potential is defined as the potential at the plain of shear. It is doubtful if the concept of the zeta potential is of assistance in describing electrokinetic phenomena as interfacial potentials are only physically meaningful in a few carefully proscribed instances. Instead, in electrophoresis, for example, all the necessary observed experimental data to define the system should be recorded and a comparison made of mobilities, other parameters being kept constant.

Introduction

MANY substances appear to acquire a surface charge when in contact with a polar liquid such as water. For example, oil droplets suspended in an aqueous electrolyte solution migrate towards the anode under the influence of an applied electric field; they seem to have acquired a net negative charge by preferentially adsorbing anions from the solution. In this case an excess surface charge has been produced by ion adsorption, but it may also be produced by ionisation, as is the case with a protein, or by the unequal dissolution of oppositely charged ions as in a silver iodide sol.

Let us consider what happens when an electric field is applied to paper discs suspended in conductivity water at 25° C. A paper disc, A, of diameter 0·5 cm, made from white commercial coating based paper coated in the laboratory with a cationic polyamine/epichlorohydrine resin, is found to move towards the cathode when an electric field is applied. If the white discs, A, are mixed with discs, B, made from coloured commercial film wrapping paper then discs A and B move towards opposite electrodes, when an electric

Under the chairmanship of A. A. Robertson field is applied, with velocities of the same order of magnitude. It is instructive to calculate the net surface charge density on such a disc.

The paper disc is probably carrying with it a sheath of water molecules. The acquired steady state velocity is the result of the compensation of two forces: an electric force $\mathbf{F}_1 = Q\mathbf{E}$, where Q is the net charge on the disc and $\mathbf{E}$ the electric field intensity, and a hydrodynamic force $\mathbf{F}_2 = -32\,\eta r\mathbf{v}/3$, where η is the viscosity of the water, r the radius of the disc and $\mathbf{v}$ its velocity. The condition $\mathbf{F}_1+\mathbf{F}_2 = 0$ gives for the net charge

$$Q = 32\eta\mathbf{v}r/3\mathbf{E}. \qquad (1)$$

Typical experimental values found were a velocity of 10^{-2} m s^{-1} for a disc of radius $2{\cdot}5\times10^{-3}$ m in an electric field of intensity 10^4 V m^{-1}. Taking $\eta = 0{\cdot}01$ P, it is found that $Q = 2{\cdot}7\times10^{-11}$ C. Hence the surface charge density $\sigma = 6{\cdot}8\times10^{-7}$ C m^{-2} and the distance apart of the charges is of the order of 5×10^4 nm (5 000 Å).

A surface excess of charge will influence the ionic distribution in the aqueous phase. Ions of opposite charge (counter-ions) will be attracted towards the surface and ions of like charge (co-ions) are repelled away from the surface. This, together with the mixing tendency of the thermal motion is thought to lead to the formation of an electric 'double layer', which consists of the charged surface and a neutralizing excess of counter-ions over co-ions distributed in a diffuse manner in the polar medium. The Gouy–Chapman–Stern theory(1–3) of the electric double layer deals with this distribution of ions and with the magnitude of the electric potentials in the locality of the charged interface. However, how did the concept of a double layer of charge at an interface come about?

The double layer

IN the original experiments of Galvani(4) and Volta(5) two discs of dissimilar metals were brought into contact, isolated and finally separated. It was shown that the discs had acquired charges of opposite sign and that it was essential to use dissimilar metals. Helmholtz(6) in 1853 introduced the concept of a double layer for the array of charges at the interface between two dissimilar metals.

Consider a plane with a uniform distribution of charge of density σ and a parallel plate at a distance d with an equal but opposite charge density $-\sigma$. Such a charge distribution is of course a double layer and the product $\sigma\times d$ was called by Helmholtz the moment of the double layer. Now by experiment it is known that the potential difference, $\Delta\Phi$, across a double layer is proportional to the moment of the double layer. Thus

$$\Delta\Phi \propto \sigma\times d \qquad (2)$$

and

$$\Delta\Phi = \sigma d/\varepsilon_r\varepsilon_0, \tag{3}$$

where ϵ_r is the relative permittivity of the medium and ϵ_0, the permittivity of a vacuum.

Consider in more detail the potential difference, $\Delta\Phi$. For a system of two phases α and β, which both contain ions of species i, a small change of the Gibbs energy in each phase is given by

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + \textstyle\sum_i \mu_i\,\mathrm{d}n_i, \tag{4}$$

so that at constant temperature and pressure

$$\mathrm{d}G = \textstyle\sum_i \mu_i\,\mathrm{d}n_i. \tag{5}$$

Suppose $\mathrm{d}n_i$ mole of ion i is transferred from phase α to phase β then the change in the net work function, $\mathrm{d}G$, can be considered to be made up of two parts. The first of these arises from the changes in the interactions of the ion with its neighbouring molecules and ions when it is transferred, i.e. it depends on the *chemical* potential difference. The second part arises from the electrical potential difference $(\Phi^\beta - \Phi^\alpha)$ between the two bulk phases.
Thus

$$\mathrm{d}G = (\mu_{ic}{}^\beta - \mu_{ic}{}^\alpha)\,\mathrm{d}n_i + (\Phi^\beta - \Phi^\alpha)z_iF\,\mathrm{d}n_i, \tag{6}$$

where z_iF is the molar electrical charge of species i. For any charged species i the chemical potential difference $\mu_{ic}{}^\beta - \mu_{ic}{}^\alpha$ cannot be measured between two phases of different chemical composition, so that $\Phi^\beta - \Phi^\alpha$ is without physical significance. However, if the two phases α and β have the *same* chemical composition then $\mu_{ic}{}^\beta = \mu_{ic}{}^\alpha$ and

$$\mathrm{d}G = (\mu_i{}^\beta - \mu_i{}^\alpha)\,\mathrm{d}n_i = (\Phi^\beta - \Phi^\alpha)z_iF\,\mathrm{d}n_i. \tag{7}$$

Therefore

$$\mu_i{}^\beta - \mu_i{}^\alpha = (\Phi^\beta - \Phi^\alpha)z_iF, \tag{8}$$

for any two phases α and β of *identical* chemical composition. This formula is the thermodynamic *definition* of the electrical potential difference between two phases of identical chemical composition.

The condition of electrical neutrality has been relaxed but the phases are required to have the same chemical composition. Is this a realistic picture? Consider a parallel plate capacitor with a plate area of 10^{-3} m^2 and a distance, d, between the plates of 10^{-2} m. The potential difference between the plates, for 10^{-10} mole of an ionic species of charge $+1$ on the positive plate, is found from (*3*) to be 10^7 V ($\epsilon_0 = 8{\cdot}85 \times 10^{-12}\ \mathrm{C^2\,J^{-1}\,m^{-1}}$). Thus a departure from electrical neutrality, corresponding to a quantity of ions far too small to be detected chemically, gives an electrostatic potential difference so large that it would only be encountered in a high tension laboratory!

Thus the μ_i's occurring in formula (*4*) have values depending on the electrical state of the phase as well as on its chemical composition, so that the μ_i of an ionic species is called its electrochemical potential. Thus an electrostatic potential difference between two phases can be defined, by applying the laws of mathematical electrostatics, for an ionic species only by excluding or ignoring differences in chemical composition between the phases. Electrons are included in the term 'ionic species'.

For the distribution of the ionic species *i* between two phases α and β of different chemical composition, the equilibrium condition is equality of the electrochemical potential, μ_i; that is to say

$$\mu_i{}^{\alpha} = \mu_i{}^{\beta}. \qquad (9)$$

Any splitting of $\mu_i{}^{\alpha} - \mu_i{}^{\beta}$ into a chemical part and an electrical part is purely arbitrary and without physical significance. The Gouy–Chapman–Stern theory of the double layer provides a basis for the interpretation of the ionic double layer potential, but it is doubtful whether there are any experimental systems on which it can be tested, since the theory arbitrarily splits the electrochemical potential into chemical and electrical components.

As long ago as 1899 Gibbs(7) wrote: 'Again, the consideration of the electrical potential in the electrolyte, and especially the consideration of the difference of potential in electrolyte and electrode, involve the consideration of quantities of which we have no apparent means of physical measurement, while the difference in potential in pieces of metal of the same kind attached to the electrodes is exactly one of the things which we can and do measure.' In other words, the electrical potential difference between two points in different media cannot be measured: it cannot be defined in terms of physical realities and is thus a concept which has no physical significance.

Now the electrostatic potential difference between two points *is* defined in electrostatics, which is concerned with the equilibrium of point charges in an electrostatic field. The surface chemist is concerned with the thermodynamic equilibrium of ions and electrons, not the electrostatic equilibrium. In a metal phase there is thermodynamic equilibrium between the electrons, metallic ions and the metal atoms; for example, for metallic silver, for the chemical potentials of each species.

$$\mu^{\mathrm{Ag}}_{\mathrm{Ag}^+} + \mu^{\mathrm{Ag}}_{e^-} = \mu^{\mathrm{Ag}}_{\mathrm{Ag}}, \qquad (10)$$

where the subscript e^- denotes electrons and the superscript denotes the phase.

All contact equilibrium is determined by the laws of thermodynamics and not the laws of electrostatics, so that only when the two phases are identical in composition can a contact potential be defined. Consider more closely the thermodynamic contact equilibrium between two phases with one common ion. Volta found that, if two different metals were placed in contact and separated, there was a difference in charge between them. For two metals, say copper and silver, in contact the electron flow takes place until the chemical potentials of the electrons are equal in both metals. This equilibrium is expressed by

$$\mu_{e^-}^{\mathrm{Cu}} = \mu_{e^-}^{\mathrm{Ag}}. \qquad (11)$$

Again for a piece of silver metal dipping into a solution, s, containing silver ions, the contact equilibrium is completely described by

$$\mu_{\mathrm{Ag}^+}^{\mathrm{Ag}} = \mu_{\mathrm{Ag}^+}^{\mathrm{s}}. \qquad (12)$$

where the metal and solution are in equilibrium with respect to silver ions only. In neither of these cases is any contact potential difference thermodynamically definable.

Consider, on the one hand, what effect is observed if a potential difference is applied across phases in contact, and, on the other hand, under what conditions phases in contact produce a potential difference. Firstly consider a potentiometer wire made of copper across which a battery is connected: between two contact points on the wire there will be a potential difference $\Phi'' - \Phi'$ equal, say, to 1 volt. At each of these contact points a piece of silver wire is connected, then

$$\mu_{e^-}^{\mathrm{Cu}''} - \mu_{e^-}^{\mathrm{Cu}'} = \mu_{e^-}^{\mathrm{Ag}''} - \mu_{e^-}^{\mathrm{Ag}'} = -F(\Phi'' - \Phi'). \qquad (13)$$

The two pieces of silver wire are dipped into two solutions of a silver salt, which have the same composition. Then

$$\mu_{\mathrm{Ag}^+}^{\mathrm{Ag}'} = \mu_{\mathrm{Ag}^+}^{\mathrm{s}'} \quad \text{and} \quad \mu_{\mathrm{Ag}^+}^{\mathrm{Ag}''} = \mu_{\mathrm{Ag}^+}^{\mathrm{s}''} \qquad (14)$$

so that

$$\mu_{\mathrm{Ag}^+}^{\mathrm{Ag}''} - \mu_{\mathrm{Ag}^+}^{\mathrm{Ag}'} = \mu_{\mathrm{Ag}^+}^{\mathrm{s}''} - \mu_{\mathrm{Ag}^+}^{\mathrm{s}'}, \qquad (15)$$

but from (*10*)

$$\mu_{\mathrm{Ag}^+}^{\mathrm{Ag}''} - \mu_{\mathrm{Ag}^+}^{\mathrm{Ag}'} = -(\mu_{e^-}^{\mathrm{Ag}''} - \mu_{e^-}^{\mathrm{Ag}'}) . \qquad (16)$$

so that

$$\mu_{\mathrm{Ag}^+}^{\mathrm{s}''} - \mu_{\mathrm{Ag}^+}^{\mathrm{s}'} = F(\Phi'' - \Phi') = F \text{ volts}. \qquad (17)$$

If the two solutions are contained in insulating vessels and the silver wires are removed then the relation (*17*) remains valid until one solution is touched by an electrical conductor. Thus the value of μ_{Ag^+} in a solution of a silver salt depends not only on the composition of the solution, but also on its electrical state, and so it is usual to refer to the electrochemical potential of an ion. Here there is a known difference of electrical potential between the two solutions of the silver salt of identical composition.

Secondly consider the system composed of two silver rods each dipped into a solution of silver nitrate of different concentration and each allowed to reach equilibrium: electrical contact between the silver nitrate solutions is then established through a membrane permeable only to silver ions. The chemical potentials of the silver ions in the two solutions are not equal as each is at a different concentration; the chemical potentials of the silver ions are equal between each piece of silver metal and its solution at equilibrium, thus

$$\mu^{\mathrm{Ag}\,''}_{\mathrm{Ag}+} = \mu^{\mathrm{s}''}_{\mathrm{Ag}+} \quad \text{and} \quad \mu^{\mathrm{Ag}'}_{\mathrm{Ag}+} = \mu^{\mathrm{s}'}_{\mathrm{Ag}+}. \qquad (18)$$

But

$$\mu^{\mathrm{Ag}''}_{\mathrm{Ag}+} - \mu^{\mathrm{Ag}'}_{\mathrm{Ag}+} = -(\mu^{\mathrm{Ag}''}_{e-} - \mu^{\mathrm{Ag}'}_{e-}) . \qquad (19)$$

and therefore

$$\mu^{\mathrm{s}''}_{\mathrm{Ag}+} - \mu^{\mathrm{s}'}_{\mathrm{Ag}+} = -(\mu^{\mathrm{Ag}''}_{e-} - \mu^{\mathrm{Ag}'}_{e-}). \qquad (20)$$

As the silver rods are two phases of the same chemical composition, Ag″ and Ag′, a potential difference may be defined between them thus

$$\mu^{\mathrm{Ag}''}_{e-} - \mu^{\mathrm{Ag}'}_{e-} = -F(\Phi'' - \Phi) = -FE, \qquad (21)$$

where E is called the electromotive force of this system. Thus the difference in chemical potential of an ion between two phases of the same ionic chemical species but of different concentration is measurable if each phase is in contact with the same chemical species, here silver metal, with which contact equilibrium can be established. This is a very limiting situation and is rarely found in the real situation in which interfacial potentials have been ‘defined’.

Having considered in just what circumstances an electrical potential difference between two phases really is definable and measurable as a physical reality, consider now the way in which it is customary to subdivide further into an ‘outer’ and a ‘surface’ potential.(8) The potential difference between the interior of two phases, $\Delta\Phi$, is called the Galvani potential or ‘inner’ potential. As has been discussed, when the two phases α and β have the same chemical composition

$$\mu_i{}^{\beta} - \mu_i{}^{\alpha} = z_i e\, \Delta\Phi. \qquad (22)$$

It is this Galvani potential difference between two phases of identical composition, which is measured by a potentiometric null method. If one of the phases is a vacuum, then it is usual to subdivide Φ for the remaining phase into two parts; one, Ψ, is considered to be due to the presence of an electrostatic charge on the surface of the phase and the other, χ, is due to the presence of a dipolar charge distribution in the surface of the phase. In other words for, say the α phase, in vacuum,

$$\Phi^{\alpha} = \Psi^{\alpha} + \chi^{\alpha}. \qquad (23)$$

Ψ^{α} is called the 'outer' or Volta potential of the phase and χ^{α}, the surface or Lange potential. When α and β are both material phases, then the Galvani potential difference may be written

$$\Phi^{\beta}-\Phi^{\alpha} = \Psi^{\beta}-\Psi^{\alpha}+\chi^{\beta}-\chi^{\alpha}. \qquad (24)$$

The 'outer' or Volta potential difference, $\Psi^{\beta}-\Psi^{\alpha}$, is readily measurable.(9) It is the so-called 'contact' potential difference, and can be measured between two different metals. However, it must be emphasized that the Volta potential difference as measured is the potential difference between two regions in free space immediately *outside* the two phases. Measurement of the Volta potential difference between two metals has been used to find the influence of a gaseous film, adsorbed on the surface of one of the metals, on the χ potential. However, as the Galvani potential difference is a physical reality only between two phases of identical chemical composition, it is not clear that the measurement of a Volta potential difference helps us in understanding an interfacial charge distribution governed by the laws of thermodynamics and not electrostatics.

For the interface between two condensed phases, it is usual to consider contributions to $\Delta\Phi$ from molecular dipoles, $\Delta\Phi_P$ and an ionic double layer, $\Delta\Phi_{\tau}$, thus

$$\Delta\Phi = \Delta\Phi_P+\Delta\Phi_{\tau}. \qquad (25)$$

The interfacial potential of the Gouy–Chapman theory is $\Delta\Phi_{\tau}$.

The Gouy–Chapman theory

CONSIDER an infinite plane surface carrying a non-discrete surface charge in contact with a solution containing ions, which are regarded as point charges. At an infinite distance from the surface, the electrical potential is equal to the inner potential of the solution, but as the surface is approached the potential changes. If the system is in electrostatic equilibrium, then the work done on the system to bring an ion from the bulk of the solution to a point near the surface is entirely due to the electrical potential difference between the initial and final positions. It is then assumed that the distribution of ions in the solution in a direction normal to the surface is given by the Boltzmann Distribution Law as

$$N_i(x) = N_i(\infty)\exp\left[-z_i e(\Phi_{\tau}(x)-\Phi_{\tau}(\infty))/kT\right], \qquad (26)$$

where $N_i(x)$ and $N_i(\infty)$ are respectively the numbers of ions per unit volume of species i, of valence z_i, at a distance x from the surface and at an infinite distance from the surface. (The Boltzmann Distribution Law gives the distribution of molecules over energy levels in a system in equilibrium at constant temperature, i.e. in thermodynamic equilibrium.)

However, for a system in electrostatic equilibrium, the relation between the space charge density, $\rho(x)$, and the potential is given by Poisson's equation,

$$\mathrm{d}^2\Phi_\tau(x)/\mathrm{d}x^2 = -\rho(x)/\varepsilon_r\varepsilon_0. \qquad (27)$$

The double layer is electrically neutral, so that the charge on the surface is balanced by the charge in the solution,

$$\sigma = -\int_0^\infty \rho(x). \qquad (28)$$

Integration of Poisson's equation for a 1:1 electrolyte, using appropriate boundary conditions, gives

$$\sigma = (8N(\infty)\varepsilon_r\varepsilon_0 kT)^{1/2} \sinh \{e(\Phi(0)-\Phi(\infty))/2kT\}. \qquad (29)$$

If $e(\Phi_\tau(0)-\Phi_\tau(\infty) \ll kT$, then (29) simplifies to

$$\sigma = \varepsilon_r\varepsilon_0\kappa(\Phi_\tau(0)-\Phi_\tau(\infty)), \qquad (30)$$

and similarly for the potential

$$\Phi_\tau(x)-\Phi_\tau(\infty) = (\Phi_\tau(0)-\Phi_\tau(\infty)) \exp(-\kappa x), \qquad (31)$$

where

$$\kappa = (2e^2N(\infty)/\varepsilon_r\varepsilon_0 kT)^{1/2}. \qquad (32)$$

(κ is the reciprocal length parameter of the Debye–Hückel theory.) According to (*31*), the decay of potential from the surface towards the bulk value $\Phi(\infty)$ is exponential. Also $\Phi_\tau(x)-\Phi_\tau(\infty)$ becomes equal to $[\Phi_\tau(0)-\Phi_\tau(\infty)]/e$ at a distance $x = 1/\kappa$ from the surface, so that κ is referred to as the 'thickness' of the double layer.

For a 1:1 electrolyte of concentration 10^{-3} mol dm^{-3}, relative permittivity 80 and temperature 25° C, κ has the value $1{\cdot}03 \times 10^8$ m^{-1}. Substitution of this value of κ into (*30*) for a cationic charge density σ of $7{\cdot}29 \times 10^{-4}$ C m^{-2}, gives a value of 10 mV for $\Phi_\tau(0)-\Phi_\tau(\infty)$. From (*31*), values of $\Phi_\tau(x)-\Phi_\tau(\infty)$ are found which on substituting into (*26*) give values of the ionic concentrations as a function of the distance x from the surface. These calculated concentration distance curves are shown in Fig. 1; anions are attracted to and cations repelled by the positively charged surface.

It is interesting to compare the distance apart of the surface charges, with those in the solution. The surface charge density was chosen so that $e[\Phi_\tau(0)-\Phi_\tau(\infty)] \ll kT$ and the simplified equations (*30*) and (*31*) could be used. The distance apart of the surface charges is 0 (15 nm). At the surface the concentration of anions is $1{\cdot}5 \times 10^{-3}$ mol dm^{-3} and so the ions are 0 (10 nm) apart. Thus although the surface charge distribution has been assumed to be non-discrete, it is quite definitely discrete. Also Poisson's equation is obtained from Coulomb's Law by assuming a continuously variable charge density ρ.

It is doubtful whether there are any experimental systems to which this

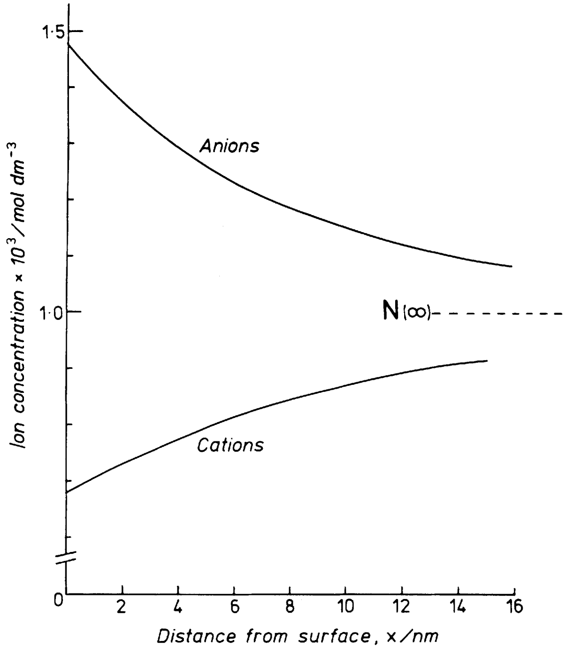

Fig. 1—The concentrations of univalent cations and anions as a function of distance from a charged surface. The bulk electrolyte concentration, $N(\infty)$, is 10^{-3} mol dm^{-3} and a value of 10 mV assumed for $\Phi_\tau(0) - \Phi_\tau(\infty)$. The relative permittivity is 80 and the temperature 25° C

theory can be applied. The potential $\Delta\Phi_\tau$ is due to the surface charge distribution; it is possible to calculate values of $\Delta\Phi_P$ from the molecular dipoles and hence a value of the Galvani potential, $\Delta\Phi$. However, as has been discussed, $\Delta\Phi$ can only be interpreted as an interfacial potential in the contact equilibrium between two phases α and β of identical chemical composition. There is no justification for ignoring the differing chemical identity of ionic species and treating the equilibrium as determined entirely by the electrostatic forces.

So much for the equilibrium situation. How does the theory of the electrical double layer help in the understanding of transport properties? Consider again the paper disc moving in the applied electric field. The net charge density on the paper disc may also be calculated using a double layer model. Consider a plane surface of an insulating material in contact with an electrolyte solution; a uniform electric field **E** is applied parallel to the surface. Ions in an element of a diffuse double layer will experience a force parallel to the surface, which is opposed by the viscous drag on either side of the element. In the steady state

$$\mathbf{E}\rho(x)\,\mathrm{d}x = \eta\left[\frac{\mathrm{d}\mathbf{v}(x)}{\mathrm{d}x}\right]_x^{x+\mathrm{d}x} = \eta\frac{\mathrm{d}^2\mathbf{v}(x)}{\mathrm{d}x^2}\,\mathrm{d}x, \qquad (33)$$

where $\rho(x)$ is the space charge density, η the viscosity, $\mathbf{v}(x)$ the velocity, and $\mathrm{d}x$ the thickness of the element. Substituting for $\rho(x)$ from Poisson's equation and integrating,

$$-\varepsilon_r\varepsilon_0\mathbf{E}\frac{\mathrm{d}\Phi_\tau(x)}{\mathrm{d}x} = \eta\frac{\mathrm{d}\mathbf{v}(x)}{\mathrm{d}x}+\text{constant}. \qquad (34)$$

The constant of integration is zero as at $x = \infty$, $\mathrm{d}\Phi/\mathrm{d}x = 0$ and $\mathrm{d}v/\mathrm{d}x = 0$. Integrating again

$$-\varepsilon_r\varepsilon_0\mathbf{E}\Phi_\tau(x) = \eta\mathbf{v}(x)+\text{constant}. \qquad (35)$$

At $x = \infty$, $\Phi_\tau(x) = \Phi_\tau(\infty)$ and $v = 0$. If the zeta potential, ζ, is defined as the potential at the surface of shear, then $\Phi_\tau(x) = \zeta$, when $v(x) = -v_\zeta$, where v_ζ is the electrophoretic velocity. If $\Phi_\tau(\infty)$ is arbitrarily taken as zero, then

$$\zeta = \eta u/\varepsilon_r\varepsilon_0, \qquad (36)$$

where u is the mobility of the plane particle.

Equation (*36*) is known as the Helmholtz–Smoluchowski equation.(10–12) The zeta potential is defined only by the boundary condition that it is the potential at the plane of shear. In order to calculate a charge density at the plane of shear it is necessary to identify this plane in the double layer theory. It cannot be the surface of the double layer as this would not be charged.

Stern suggested a modification to the double layer model to allow for the fact that at short distances from the surface there may exist a specific 'chemical' interaction between the ions and the surface. These strongly adsorbed ions are attached to the surface by electrostatic and van der Waals forces strongly enough to overcome thermal agitation. The double layer is then considered to be divided into two parts separated by a plane (the Stern plane), located at about a hydrated ion radius from the surface. The specifically adsorbed ions are located in the Stern layer, that is between the surface and the Stern plane. Ions with centres located beyond the Stern plane form the diffuse part of the double layer to which the Gouy–Chapman theory is considered to be applicable. The potential changes from $\phi(0)-\Phi(\infty)$ at the surface to $\Phi(\delta)-\Phi(\infty)$ in the Stern layer and from $\Phi(\delta)-\Phi(\infty)$ to zero in the diffuse double layer.

At low potentials when $e(\Phi_\tau(\delta)-\Phi_\tau(\infty)) \ll kT$, then (*30*) is applicable to the diffuse layer and the surface charge at the Stern plane is given by

$$\sigma_\delta = \varepsilon_r\varepsilon_0\kappa(\Phi_\tau(\delta)-\Phi_\tau(\infty)). \qquad (37)$$

If it is assumed that the plane of shear in an electrokinetic experiment is the Stern plane and $\Phi_\tau(\delta)$ replaced by the zeta potential, ζ, then, if $\Phi_\tau(\infty)$ is arbitrarily assumed to be zero,

$$\sigma_\zeta = \varepsilon_r \varepsilon_0 \kappa \zeta. \qquad \qquad (38)$$

This equation has the same form as (*3*), the relationship between surface charge density and potential for a parallel plate capacitor with the distance between the plates equal to $1/\kappa$. Following Helmholtz, the moment of the double layer is given by σ_δ/κ. Substituting for ζ from (*36*) gives

$$\sigma_\zeta = u\eta\kappa. \qquad \qquad (39)$$

For the paper disc with mobility $u = 10^{-6}\,\mathrm{m^2\,s^{-1}\,V^{-1}}$, $\eta = 0{\cdot}01$ P and $\kappa = 1{\cdot}03 \times 10^7\,\mathrm{m^{-1}}$ (the conductivity water is assumed to have a 1:1 electrolyte concentration of $10^{-5}\,\mathrm{mol\,dm^{-3}}$) then $\sigma_\zeta = 1{\cdot}03 \times 10^{-2}\,\mathrm{C\,m^{-2}}$. This is equivalent to 6×10^{16} elementary charges per square metre with a distance apart of 0 (4 nm). The values for the surface charge density calculated by the two methods differ by a factor of 10^4!

However, the situation is even worse. If (*36*) is used to calculate a value of zeta, it is found to be 1·4 V. Thus $e\zeta \gg kT$ and (*29*) must be used to calculate σ_ζ. This gives a figure of $1{\cdot}5 \times 10^8\,\mathrm{C\,m^{-2}}$!

Both methods of calculation should give the charge density at the plane of shear. There is a serious inconsistency between the two methods. The first method is open to the objection that mobility and temperature are measured, but the viscosity of the system is not simultaneously measured, i.e. the system is not well defined. However, the Smoluchowski equation also contains the viscosity. The difference between the two methods lies in interpreting a macroscopic transport process at the molecular level: in other words in the concept of the zeta potential.

The zeta potential

THE paradox of the zeta potential is that here is a readily calculable property of the system, which is not readily interpretable in terms of a physical reality. It certainly cannot be a measure of the interfacial potential in the system; the limited circumstances in which an interfacial potential can be measured as a defined physical quantity have already been discussed. The zeta potential is defined only by the boundary conditions on (*35*) as the potential at the plane of shear. Does zeta have any physical significance and what is the precise location of the plane of shear?

In the derivation of (*36*) Poisson's equation is used; in other words a continuous charge distribution is assumed. A steady state is considered to be set up between the mechanical and electrical forces and this, by implication, is interpreted at the molecular level in terms of the shear plane. In electrophoresis the system is in a steady state not only in a constant electric field but also in a constant temperature field.(13)

Possibly the Gouy–Chapman–Stern theory of the double layer has held favour for so long, because of the limited success of the Debye–Hückel theory for strong electrolytes. But it must be remembered that this latter theory is concerned with calculating measurable mean ionic chemical potentials, and not indefinable interfacial potentials. Also by *definition* the whole of the electrostatic interaction is given by the Debye–Hückel $\ln \gamma \pm$ so that a term for the chemical interaction of the ions, $\ln \gamma_c$, may be added if so wished.

In an electrokinetic experiment it is necessary to record all the measured and known state functions to specify the system completely. The minimum data necessary to calculate the thermodynamic functions of the system must be recorded. A model of the system may then be assumed to calculate these properties. When agreement is reached between theory and experiment it may be hoped that the model indeed presents a picture of the system on a molecular level. Until the necessary statistical mechanical theory is available, obsession with parameters like the zeta potential leads to the delusion that it is a real thermodynamic property of the system. In electrophoresis measured mobilities should be recorded in a system of adequately described state variables (temperature, electric field etc.) sufficient to define the system completely. The laws of mechanics and electrostatics cannot be applied to electrokinetic phenomena and yet the overwhelming criterion of the constancy of temperature is ignored. Ionic movement in these systems is determined by the electrochemical potentials and not the electrostatic potential difference.

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Transcription of Discussion

Discussion

Prof. J. T. G. Overbeek One of the things we want to do when we observe electro-kinetic phenomena is to explain them in a way that we think is based on simple things like charges or maybe electrostatic or electrochemical potentials. Now, one thing is that if you stop at noting the mobility as such and do not try to bring these back to the charges carried by the particles or the ions I think that you cannot make much progress. I quite agree with you that it would be nicer to base the whole theory of conductivity on irreversible thermodynamics and some progress has been made in that field. Although electrokinetic phenomena can be attacked to some extent by irreversible thermodynamics I may just mention a few reasons why the zeta potential is still an important quantity. We observe a mobility and we calculate a potential in a well explained way. Then we find, except perhaps for the case that Dr Corte has shown, that the zeta potential is always a fraction, quite often a small fraction, of what we know the interfacial potential to be. Now of course I have to say what I mean by interfacial potential between two different phases. That is the difference when the two are non-charged. Quite often we can determine the point of zero charge as for the mercury/water, silver iodide/water and many cases of oxide/water interfaces. We have not the slightest knowledge whether the interfacial potential is zero when the charge of the surface is zero or whether it has a finite magnitude. But starting from the zero point of charge we can measure the change in interfacial potential by relatively simple electrochemical means, just as we can measure pH which is just as well defined or you may say just as not quite accurately defined. If we don't want to talk about the zeta potential we must also scratch our heads about the pH. In quite a number of cases charges calculated by zeta potential can be compared with the surface charge measured chemically by determining the number of ions of unit charge so that we can calculate an adsorbed or dissociated charge and you find then that the electrokinetic charge is smaller, but not much smaller than that. The second reason why zeta potential and double layer concepts are important is that otherwise it is very difficult to understand why any electrolyte that doesn't seem to have any affinity to the

Under the chairmanship of A. A. Robertson surface nevertheless affects electrokinetic experiments very much. In the concept of the double layer, and again it doesn't matter whether you apply it to a single ion or a surface, this becomes clear because the counter charge comes closer to the central charge and both relaxation and hydrodynamic effects which are working against mobility become larger. I still feel that the way we deal with electrokinetic phenomena is a good way although it is certainly not the last word in that field and further work for instance by irreversible thermodynamics would be nice. Electro-osmosic and streaming potential have been quite well related by irreversible thermodynamics, but electrophoresis and sedimentation potential only in the case of simple systems.

Hardman Thank you, the point I was trying to make is that I completely agree that with measurements of macroscopic physical properties we should always endeavour to get an interpretation at a molecular level. But when I compare papers in my own field of the thermodynamics of mixtures where we measure the thermodynamic properties of a system, and that is the major part of the paper, then we all feel that we have to try to interpret other peoples' theories of mixture of fluids and try to get some molecular parameters out of them. It seems to me as an outsider in this field that the emphasis here, with electrophoresis, has gone completely the other way and the title of a paper may almost be, for example, 'the calculation of the zeta potential' of a particular system whereas the purpose of the experiment is the observation of mobilities and then to get into the right perspective the interpretation of these measurements at the molecular level.

Dr A. H. Nissan I have a question for Dr Hardman. You have explained very well in the paper that certain people in dealing with electrostatics are not being precise enough because they do not take chemical potential into account. This is good but we are discussing dissipative phenomena in electrophoresis, and frankly when I read the paper I wondered why the thermodynamics of reversible processes was used as an introduction to electrophoresis which I believe, although I am not a thermodynamicist, could not be used to explain this phenomenon. I was very delighted when in your presentation you warned us to ignore the expectation that the thermodynamics of reversible processes would explain electrophoresis since there was energy dissipation. But, Dr Hardman, you haven't given us anything against what Dr Overbeek has told us; you just implied that you don't like it. That's all right; every scientist is entitled to like or dislike anything in science. I just wanted to make sure whether my understanding was correct.

Hardman That was not my intention. If we are talking about irreversible thermodynamics, the zeta potential does not come out of the elegant equations. For example, if you refer to Guggenheim 'Thermodynamics', 1967, 5th edition, p. 369, the cross-coefficient L_{21} directly give us the mobility, there is no mention of the zeta potential. What I was talking about was irreversible statistical mechanics which is still in its infancy and needs further work to be done.