

# Electrical properties of interfaces

## Nomenclature

|            |                                                       |
|------------|-------------------------------------------------------|
| $a$        | radius of sphere                                      |
| $a_i$      | activity of ion $i$                                   |
| $C_\delta$ | capacitance of Stern layer                            |
| $c_i$      | molar concentration of ion $i$                        |
| $e$        | electron charge                                       |
| $E$        | electric field strength                               |
| $E_S$      | streaming potential                                   |
| $F$        | Faraday constant                                      |
| $i$        | current                                               |
| $I_S$      | streaming current                                     |
| $k$        | Boltzmann constant                                    |
| $n_+, n_-$ | local number concentrations of cations and anions     |
| $n_0$      | number concentration of ions in bulk solution         |
| $n_i$      | local number concentration of ion $i$                 |
| $n_{i0}$   | number concentration of ion $i$ in bulk solution      |
| $N_S$      | surface density of adsorption sites                   |
| $q$        | total charge on sphere                                |
| $Q$        | flow rate                                             |
| $r$        | radial distance from centre of sphere                 |
| $R$        | gas constant                                          |
| $T$        | absolute temperature                                  |
| $U$        | electrophoretic mobility                              |
| $u_i$      | specific adsorption potential of ion $i$              |
| $v$        | velocity                                              |
| $v_{eo}$   | electro-osmotic velocity                              |
| $x$        | distance from surface                                 |
| $X$        | $= \kappa x$                                          |
| $x_i$      | mole fraction of counterions in solution              |
| $y$        | $= ze\psi/kT$                                         |
| $y_0$      | $= ze\psi_0/kT$                                       |
| $z$        | valence of ions in symmetrical ( $z-z$ ) electrolyte. |
| $z_i$      | valence of ion $i$ (including sign of charge)         |
| $\gamma$   | $= \tanh(y_0/4)$                                      |
| $\delta$   | thickness of Stern layer                              |
| $\Delta P$ | pressure difference                                   |

|                 |                                               |
|-----------------|-----------------------------------------------|
| $\epsilon$      | permittivity                                  |
| $\zeta$         | zeta potential                                |
| $\kappa$        | Debye–Hückel parameter, eqn (2.7)             |
| $\lambda_0$     | specific conductivity of solution             |
| $\lambda_s$     | surface conductivity                          |
| $\mu$           | viscosity                                     |
| $\rho$          | volume charge density in solution             |
| $\sigma_\delta$ | charge density in the Stern layer             |
| $\sigma_0$      | surface charge density                        |
| $\sigma_1$      | diffuse layer charge per unit area of surface |
| $\psi$          | electrical potential                          |
| $\psi_0$        | surface potential                             |

## 2.1 INTRODUCTION

Many of the important properties of colloidal systems are determined directly or indirectly by the interaction forces between particles. These colloidal forces consist of several components, principally the electrical double layer, van der Waals, Born, hydration and steric forces, which act over relatively short distances and are greatly dependent on the surface properties of particles or collectors. Consequently, a detailed understanding of the solid–liquid interfacial region is important in any attempt to model and simulate aggregation and deposition phenomena. The nature of the forces will be discussed in further detail in Chapter 3, while this chapter will focus on the nature of charged interfaces.

Electrical interaction between colloidal particles (especially in aqueous systems) is one of the most important influences on particle stability, aggregation and deposition. Most particles in aqueous media are charged, for reasons which will be considered briefly in Section 2.2.1. In an electrolyte solution, the distribution of ions around a charged particle is not uniform and gives rise to an *electrical double layer*. This topic has been the subject of several reviews, including the comprehensive texts of Hunter (1981,1987) and Lyklema (1991) and others cited in the bibliography. The essential point is that the charge on, say, a particle surface is balanced by an equivalent number of oppositely charged *counterions* in solution. These counterions are subject to two opposing influences: electrostatic attraction tending to localize the counterions close to the particles and the tendency of ions to diffuse randomly throughout the solution, owing to their thermal energy. The surface charge on a particle and the associated counterion charge together constitute the electrical double layer. The surface charge and the distribution of counterions near to the surface depend greatly on the nature and concentration of salts in solution, giving a relatively simple means of modifying colloid interactions. In most cases, the only practical means of manipulating the stability of particles and their tendency to deposit on surfaces is by changing the electrical interaction through changes in the solution chemistry.

For this reason, it is worthwhile to outline the important properties of the electrical double layer, and to show how physical models can be applied. It will

become apparent that although modern experimental techniques and computational tools have given a better insight into charged interfaces and the various colloidal forces, a complete analysis is not usually possible in real systems. It is nearly always necessary to resort to approximate expressions, which prove to be convenient and reasonably accurate for many practical purposes. It is helpful to appreciate the limitations of these expressions which may form the basis for later modelling and simulation strategies.

## 2.2 The electrical double layer

### 2.2.1 Origin of surface charge

When two dissimilar phases are in contact it is likely that there will be a separation of charge and a difference in electrical potential between them. If we restrict attention to the case of a solid in contact with an aqueous electrolyte solution, there are several possible mechanisms for the separation of charge:

- (a) a difference in affinity of ions for the two phases
- (b) ionization of surface groups
- (c) physical restriction of certain ions to one phase.

In the important case of ionic solids, one or other of the constituent ions may have a greater tendency to dissolve in the aqueous phase. Examples include the extensively studied cases of silver halide suspensions (Bijsterbosch and Lyklema, 1978), the best known example being *silver iodide*. In contact with pure water, silver ions have a greater tendency to escape from the crystal lattice, leaving a crystal with an excess negative charge. The solubility product of silver iodide is about  $10^{-16} (\text{mol dm}^{-3})^2$ . If the concentration (strictly, *activity*) of silver ions in solution is increased (and hence the iodide concentration decreased), a point is reached where the greater escaping tendency of the silver ions is just balanced by their higher concentration in solution, and the solid then has no net charge. This is the *point of zero charge (PZC)* and occurs when the silver concentration is about  $3.26 \times 10^{-6} \text{ mol dm}^{-3}$  or  $\text{pAg} = 5.5$  (and hence  $\text{pI} = 10.5$ ).

Because the surface electrical properties of ionic solids such as silver iodide are dependent on the concentrations of the constituent ions, these are known as *potential-determining ions (PDI)*. The relationship between the surface potential,  $\psi_0$ , and the concentration of PDIs can be derived by straightforward thermodynamic reasoning and the result is known as the *Nernst equation*:

$$\psi_0 = \text{constant} + \left( \frac{RT}{z_i F} \right) \ln a_i \quad (2.1)$$

where  $R$  is the gas constant,  $T$  the absolute temperature and  $F$  the Faraday constant.  $z_i$  and  $a_i$  are the valence and the activity of the PDI,  $i$ .

At low electrolyte concentrations the ion activity can be approximated by the concentration,  $c_i$  and in this case eqn (2.1) can be differentiated to give:

$$\frac{d\psi_0}{d(\log_{10} c_i)} = 2.303 \frac{RT}{z_i F} \left( = \frac{59.2}{z_i} \text{ mV at } 25^\circ\text{C} \right) \quad (2.2)$$

Thus, for a singly charged PDI, the potential of the solid should change by about 59 mV for a ten-fold variation in concentration. Note that the term  $z_i$  in these expressions must include the sign of ion charge, so that for a positive PDI the potential will *increase* for an increase in concentration and vice versa.

Other ionic solids which show similar behaviour include calcium carbonate, where the PDIs are  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$ . However, in this case there are complications caused by the reaction of the carbonate ion to form  $\text{HCO}_3^-$  and  $\text{H}_2\text{CO}_3$ , depending on the pH (Thompson and Pownall, 1989). This gives an apparent pH dependence of surface charge, but  $\text{H}^+$  is not a PDI in the conventional sense.

Another very important example of pH-dependent surface charge is the case of metal oxides, such as  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$ . In contact with water, the oxide surfaces become hydroxylated, giving the possibility of surface ionization to yield either positive or negative groups. In a simplified manner, the ionization of such groups can be written as (Stumm, 1992):



where S denotes a solid surface.

The process occurring from left to right involves the progressive loss of two protons, and the steps can be characterized by appropriate equilibrium constants  $K_1$  and  $K_2$ . The extent of deprotonation depends on the values of these constants and on the pH of the solution. As the pH is increased there is a greater tendency to lose protons and the oxide surface becomes more negative. There is a characteristic pH value at which the surface has no net charge and this can also be termed the PZC, by analogy with the case of ionic solids discussed above. Because of the nature of the oxide surface charge, experimental determination of surface charge densities and PZC values can be carried out fairly simply by acid-base titration.

According to the simplest model of the oxide-water interface, the PZC is just the mean of  $\text{p}K_1$  and  $\text{p}K_2$ . These depend very much on the chemical nature of the oxide. Acidic materials such as silica (PZC about 2) have a great tendency to lose protons and are negatively charged over most of the pH range. Basic oxides such as MgO (PZC about 12) acquire protons very readily and are positively charged at most pH values. Intermediate cases include  $\text{Fe}_2\text{O}_3$  (PZC 6.8) and  $\text{TiO}_2$  (PZC 6.2), where the surface charge can change sign as a result of quite small pH changes in the neutral region. Such considerations are of great practical importance in the aggregation and deposition of oxide particles.

The description given above is highly simplified and more refined models are available (Hiemstra and van Riemsdijk, 1991). In particular, it should be noted that PZC values for oxides are dependent on such factors as crystalline form and mode of preparation. Literature values should be treated with some caution. Although  $\text{H}^+$  and  $\text{OH}^-$  are not strictly constituent ions of oxides, the change of surface potential with pH can show Nernstian behaviour, especially in the region of the PZC.

Some surfaces have only monofunctional ionic groups, such as latex particles with carboxylic and sulphate groups. In these cases, the degree of ionization, and hence the surface charge density, may be dependent on pH, but there is no PZC. The surface charge approaches zero as the pH is changed, but does not reverse.

Preferential adsorption of ions on surfaces may occur and modify the surface charge. In the case of ionic surfactants, hydrophobic interaction can give strong adsorption and the surface acquires a charge characteristic of the surfactant ion. However, in practice, the more usual case is where anions or cations from solution adsorb on charged surfaces. This will be discussed in the context of electrical double layer models in Section 2.2.3.

The examples given so far fall into categories (a) and (b) listed at the beginning of this section. In many important cases, such as oxides, it is difficult to distinguish the concepts of surface ionization and different affinities of ions for the solid surface.

The third category is rather different and includes materials with an 'inherent' excess charge as a result of isomorphous substitution. For instance in the tetrahedral silica layer of kaolinite, substitution of Si(IV) by Al(III) gives a net negative lattice charge. For similar reasons, many clay minerals in water are negatively charged.

## 2.2.2 The Gouy–Chapman double layer model

Whatever the origin of the surface charge, it must be exactly balanced by an equal and opposite charge in solution. This balancing charge is accounted for by an excess number of oppositely charged ions or *counterions* in the solution adjacent to the charged surface and a deficit of similarly charged ions or *co-ions*. The question now is how is this charge distributed in the solution?

Considering, for simplicity, a planar interface of infinite extent, with a surface potential  $\psi_0$  (V) and a surface charge density  $\sigma_0$  ( $\text{C m}^{-2}$ ), it is possible to describe the distribution of charge and potential in the solution as a function of distance from the surface. An approach due, independently, to Gouy and Chapman (see, for example Hunter, 1981) is based on a number of simplifying assumptions:

- (a) an infinite, flat impenetrable interface
- (b) ions in solution are point charges, able to approach right up to the interface
- (c) the surface charge and potential are uniformly 'smeared out' over the surface
- (d) the solvent is a uniform medium with properties (especially permittivity) that are independent of distance from the surface.

Assumptions (a)–(d) are all questionable and can be modified in refined versions of the theory. The assumption of a 'smeared-out' surface charge may seem especially suspect in view of known charging mechanisms which involve discrete ionic sites. However, the rate of exchange of protons and other ions between surface sites and the adjacent solution is usually very rapid, compared

to, say, the time of approach of colloidal particles. For this reason, many surfaces may be regarded as having an effectively uniform surface charge density.

A fundamental result from electrostatics gives the relationship between charge density,  $\rho$  ( $\text{C m}^{-3}$ ), and potential,  $\psi$ , at any point. This is the *Poisson equation*:

$$\nabla^2 \psi = -\frac{\rho}{\epsilon} \quad (2.3)$$

where  $\epsilon$  is the permittivity of the medium.

In an electrolyte solution the charge density depends on the local concentrations of anions and cations and these depend on the local potential through the *Boltzmann expression*:

$$n_i = n_{i0} \exp \left( -\frac{z_i e \psi}{kT} \right) \quad (2.4)$$

where  $n_i$  is the number concentration of ion  $i$  at a point where the potential is  $\psi$ ,  $n_{i0}$  is the corresponding concentration in the bulk solution (where the potential is zero),  $e$  is the electron charge and  $k$  is the Boltzmann constant.

The exponential term represents the electrical energy of an ion with a charge  $z_i e$ , relative to its thermal energy  $kT$ . If the ion has a charge opposite to the sign of the potential, then the local concentration will be higher than the bulk value and vice versa. Thus, when the potential has a negative sign, there will be a local excess of cations and a deficit of anions. It is convenient to restrict attention to symmetrical,  $z-z$ , electrolytes and in this case the charge density is given simply by:

$$\rho = ze(n_+ - n_-) = -2zen_0 \sinh \left( \frac{ze\psi}{kT} \right) \quad (2.5)$$

where  $n_+$  and  $n_-$  are the local number concentrations of anions and cations and  $n_0$  is the number concentration of each ion in the bulk solution. In this case  $z$  is the charge number of the ions and does not include the sign of charge.

Since we are considering a flat interface and are only concerned with the variation of potential normal to it, the one-dimensional form of the Poisson equation can be used, which, together with eqn (2.3), gives the *Poisson-Boltzmann expression*:

$$\frac{d^2 \psi}{dx^2} = \frac{2zen_0}{\epsilon} \sinh \left( \frac{ze\psi}{kT} \right) \quad (2.6)$$

It is convenient to introduce the dimensionless parameters:

$$y = ze\psi/kT \quad \text{and} \quad X = \kappa x$$

where  $\kappa$  is given, for  $z-z$  electrolytes, by:

$$\kappa^2 = \frac{2e^2 n_0 z^2}{\epsilon kT} \quad (2.7)$$

The *Debye-Hückel parameter*,  $\kappa$ , has the dimensions of reciprocal length and plays a very important part in electrical interaction between colloidal particles.

Substituting  $y$  and  $X$  in eqn (2.6):

$$\frac{d^2y}{dX^2} = \sinh y \quad (2.8)$$

This form of the Poisson–Boltzmann expression can easily be solved, with the following boundary conditions (since the potential takes the value  $\psi_0$  at the surface and zero in the bulk solution, far from the surface):

$$y = y_0 (= ze\psi_0/kT) \quad \text{when } X = 0; \quad y = 0 \quad \text{and } dy/dX = 0 \quad \text{when } X = \infty$$

The solution of eqn (2.8) is then:

$$y = 2 \ln \left[ \frac{1 + \gamma \exp(-X)}{1 - \gamma \exp(-X)} \right] \quad (2.9)$$

where  $\gamma$  is a function of the dimensionless surface potential,  $y_0$ :

$$\gamma = \frac{\exp(y_0/2) - 1}{\exp(y_0/2) + 1} = \tanh \left( \frac{y_0}{4} \right) \quad (2.10)$$

There are two useful approximations to eqn (2.9). If the surface potential is quite low ( $y_0 < 1$  or  $\psi_0$  less than about 25 mV in 1–1 electrolytes), then a simple exponential form is appropriate:

$$y = y_0 \exp(-X); \quad \text{or } \psi = \psi_0 \exp(-\kappa x) \quad (2.11)$$

This can be also be obtained directly by solving the linear form of eqn (2.8), i.e. assuming  $\sinh y \approx y$ , and is often known as the *Debye–Hückel approximation*. Actually, eqn (2.11) is an adequate approximation to eqn (2.9) for values of  $y_0$  up to about 2.

For any value of surface potential, at points not too close to the surface ( $X > 1$ ), another exponential form is suitable:

$$y = 4\gamma \exp(-\kappa x) \quad (2.12)$$

Since, for  $y_0 < 1$ ,  $\gamma \approx y_0/4$ , eqn (2.12) becomes equivalent to eqn (2.11) for low values of surface potential. Eqn (2.12) is the basis of the ‘linear superposition’ approximation for the interaction of charged particles (see Section 3.2.1).

The approximate exponential fall of potential from a charged surface means that the Debye–Hückel parameter,  $\kappa$ , defined in eqn (2.7) for  $z$ - $z$  electrolytes, determines the extent of the counterion charge in solution (or the *diffuse layer*). At a distance  $1/\kappa$  from the surface the potential has fallen to a value  $1/e$  ( $1/2.72$ ) of the surface potential. For this reason, the length  $1/\kappa$  is usually known as the ‘thickness’ of the diffuse layer. For the general case of electrolyte solutions containing a number of dissolved salts,  $\kappa$  is defined by:

$$\kappa = \sqrt{\left( \frac{e^2 \sum n_{i0} z_i^2}{\epsilon kT} \right)} \quad (2.13)$$

where the sum is taken over all ions present in the solution.

Inserting numerical values appropriate to aqueous solutions at 25°C and converting the ion concentrations into molar terms gives:

$$\kappa = 2.32 \times 10^9 (\sum c_i z_i^2)^{1/2} \quad (2.14)$$

where the ion concentrations  $c_i$  are in  $\text{mol dm}^{-3}$  and  $\kappa$  is in  $\text{m}^{-1}$ .

For typical solutions, values of the diffuse layer thickness,  $1/\kappa$ , are in the range 1–100 nm. For instance, in  $10^{-4} \text{ M NaCl}$  the value is about 30 nm and in  $10^{-4} \text{ M CaSO}_4$  about 15 nm. These values are indicative of the range of electrical interaction between colloidal particles.

Another important result from Gouy–Chapman theory relates the surface charge density,  $\sigma_0$ , to the surface potential,  $\psi_0$ . The former is easily derived, since the surface charge must be balanced by the excess charge in the diffuse layer. Considering unit area of surface, the total diffuse layer charge is derived simply by integration of the charge density given by eqn (2.5):

$$\sigma_0 = - \int_0^\infty \rho \, dx$$

It can be shown that, for symmetrical electrolytes, the result is given by (Hiemenz, 1985):

$$\sigma_0 = (8n_0 \epsilon kT)^{1/2} \sinh \left( \frac{y_0}{2} \right) \quad (2.16)$$

For small potentials ( $y < 1$ ), this simplifies to:

$$\sigma_0 = \epsilon \kappa \psi_0 \quad (2.17)$$

If the double layer system is regarded as a parallel-plate capacitor, then the capacitance is simply  $\epsilon \kappa$  and  $1/\kappa$  is the effective distance between the plates. This is another reason why the length  $1/\kappa$  can be thought of as the ‘thickness’ of the diffuse layer.

The Gouy–Chapman theory, as described briefly above, has several shortcomings. For instance, measured capacitances at certain interfaces can be much lower than those predicted by the theory. Also, counterion concentrations close to charged interfaces, calculated from eqn (2.4), can become unreasonably high, even for only moderate values of surface potential. Quite simple modifications to the theory can be made, the most important of which are to allow for *finite ion size* and *specific adsorption of ions*, which lead to the *Stern* and *Stern–Grahame* models of the double layer.

### 2.2.3 The Stern model

Ions in solution are not point charges, but have a finite size. Hydrated ions have diameters typically of the order of 0.5 nm or less and allowance for the size is probably the most important correction to the Gouy–Chapman theory. If we think of the ion charge as being located at the centre of a sphere of finite size, then the charge cannot touch the interface, but must be limited to a distance of

approach equal to the sphere radius. This distance is usually given the symbol  $\delta$  and it defines a region which is inaccessible to counterion charge. This concept, originally due to Stern, accounts for many of the observed discrepancies with Gouy–Chapman theory. The plane at distance  $\delta$  from the surface is usually known as the *Stern plane*, and the region between this plane and the surface is known as the *Stern layer*. Outside the Stern layer there is a diffuse layer of counterions, just as in the Gouy–Chapman model.

In the simplest Stern model, counterions are entirely mobile and not adsorbed on the surface. In this case there is no charge in the Stern layer and the diffuse layer charge just balances the surface charge. The Stern plane can be regarded as a capacitor, with a capacitance which depends on its thickness,  $\delta$ , and the permittivity of the medium close to the surface. In aqueous systems the permittivity of water close to a charged interface may not be the same as the bulk value, but could be significantly lower as a result of the high field strength. The relative permittivity (dielectric constant) of bulk water is quite high (about 78) because of the highly polar nature of the water molecule. In high field strengths, most of the water dipoles become orientated in the field and the dielectric constant can be reduced to a value as low as 6 for the case of electric saturation (Hiemstra and van Riemsdijk, 1991). It is likely that the bulk value would be reached at a distance of only one or two hydrated ion diameters from the surface. If we assume  $\delta = 0.3$  nm and a value of 10 for the dielectric constant of water in the Stern layer, then the inner layer capacitance turns out to be about  $0.3 \text{ F m}^{-2}$ , which is comparable to values found for silver iodide.

In the case of low surface potential, the capacitance of the diffuse layer can be calculated from eqn (2.17) and becomes greater at higher ionic strengths (higher  $\kappa$ ). For instance, in  $10^{-1} \text{ M}$  1–1 salt solution, the diffuse layer capacitance would be about  $0.7 \text{ F m}^{-2}$ , which is rather higher than the Stern layer capacitance calculated above. Two capacitors in series have a total capacitance,  $C_t$  given by:

$$\frac{1}{C_t} = \frac{1}{C_1} + \frac{1}{C_2} \quad (2.18)$$

The total capacitance cannot exceed the smaller of the two individual values, which means that in the example above the total capacitance would be mainly determined by the Stern layer value. In dilute salt solutions, where the diffuse layer capacitance is much lower, this determines the overall value. The surface potential,  $\psi_0$ , falls to zero in the bulk solution and this drop is divided between the Stern and diffuse layers according to their capacitances. The largest potential drop occurs over the layer with the smallest capacitance, so that at high ionic strength the potential will fall sharply through the Stern layer, to the value  $\psi_\delta$  (the *Stern potential*). In very dilute salt solutions, where the diffuse layer capacitance is smaller than that of the Stern layer (which is largely independent of ionic strength), most of the potential drop occurs over the diffuse layer and the Stern potential has a value close to the surface potential  $\psi_0$ .

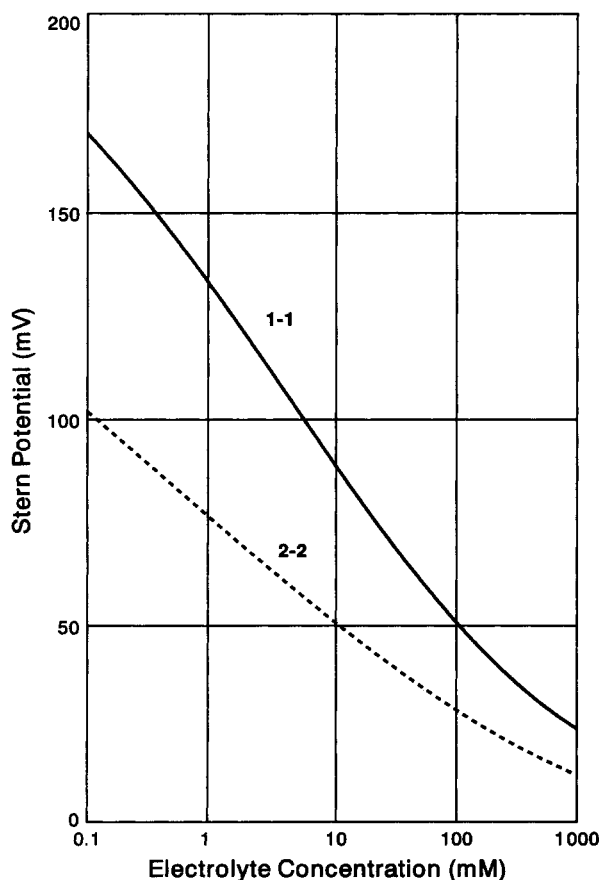
If the Stern layer has no adsorbed ions (see below), then the diffuse layer charge is equal and opposite to the surface charge and is given by an expression analogous to eqn (2.16), but with the Stern layer potential in place of the surface potential. The potential drop across the Stern layer can then be calculated from

the charge, if the Stern layer capacitance  $C_\delta$  is known. With numerical values appropriate to aqueous solutions at 25°C, the result is:

$$\psi_0 - \psi_\delta = \frac{0.117}{C_\delta} c^{1/2} \sinh(19.4z\psi_\delta) \quad (2.19)$$

where  $c$  is the concentration of  $z$ - $z$  electrolyte ( $\text{mol dm}^{-3}$ ).

Results from this expression are shown in Figure 2.1, where a surface potential of 250 mV and a Stern layer capacitance of  $0.2 \text{ F m}^{-2}$  have been assumed. The Stern potential  $\psi_\delta$  is plotted against concentration of 1-1 and 2-2 salts. The Stern potential falls with increasing salt concentration and has lower values in the case of more highly charged ions.



**Figure 2.1** The variation of Stern potential,  $\psi_\delta$ , with the concentration of symmetrical 1-1 and 2-2 electrolytes. The surface potential,  $\psi_0$ , is assumed to be 250 mV and the Stern layer capacitance is  $0.2 \text{ F m}^{-2}$

The fact that the Stern potential is often much lower than the true surface potential has several important implications. One of these is that the diffuse layer can often be modelled quite well with the linear Poisson–Boltzmann (low-potential) approximation, where this would not be suitable if the surface potential were used.

The counterions may not be entirely mobile, but could be bound to the surface, to some extent. The electrical energy of an ion in the Stern plane, relative to the thermal energy, is  $ze\psi_\delta/kT$ . For univalent ions and Stern potentials greater than about 50 mV, this term becomes significant and may be responsible for some counterion binding to the surface. This is analogous to ion pair formation in electrolyte solutions (Davies, 1962).

There may also be non-electrostatic (or ‘chemical’) reasons for binding of ions, and the effect is then often known as *specific adsorption*. Although there is some confusion over this term, it draws attention to an important distinction. If a metal ion is to undergo specific binding to a surface, it is usually necessary for some water of hydration to be lost. There can then be direct bond formation between the metal and electron-donating groups on the surface (e.g. oxygen groups at an oxide surface). Such an interaction is said to lead to an *inner sphere complex*, as opposed to an *outer sphere complex* formed between a hydrated metal ion and a charged surface (Stumm, 1992). It is reasonable to suppose that outer sphere complexes are formed entirely as a result of electrostatic attraction. However, even ions forming outer sphere complexes can show ‘specific’ differences as a result of different sizes of the hydrated ions.

Strictly, the division of an interaction energy into ‘electrical’ and ‘chemical’ terms is not justified thermodynamically, but it is conceptually appealing and double layer models are often formulated in this way. The energy appearing in the Boltzmann expression then takes the form  $(ze\psi_\delta/kT + u)$ , where  $u$  is the *specific adsorption potential*. When this term exceeds a few  $kT$  units, it can dominate the electrical term. Using an approach similar to that of the Langmuir adsorption isotherm, it is possible to calculate the surface concentration of adsorbed counterions, which, when converted to an equivalent charge density in the Stern layer,  $\sigma_\delta$ , becomes (Hunter, 1993):

$$\sigma_\delta = z_i e N_s x_i \exp \left[ - \frac{(z_i e \psi_\delta + u_i)}{kT} \right] \quad (2.20)$$

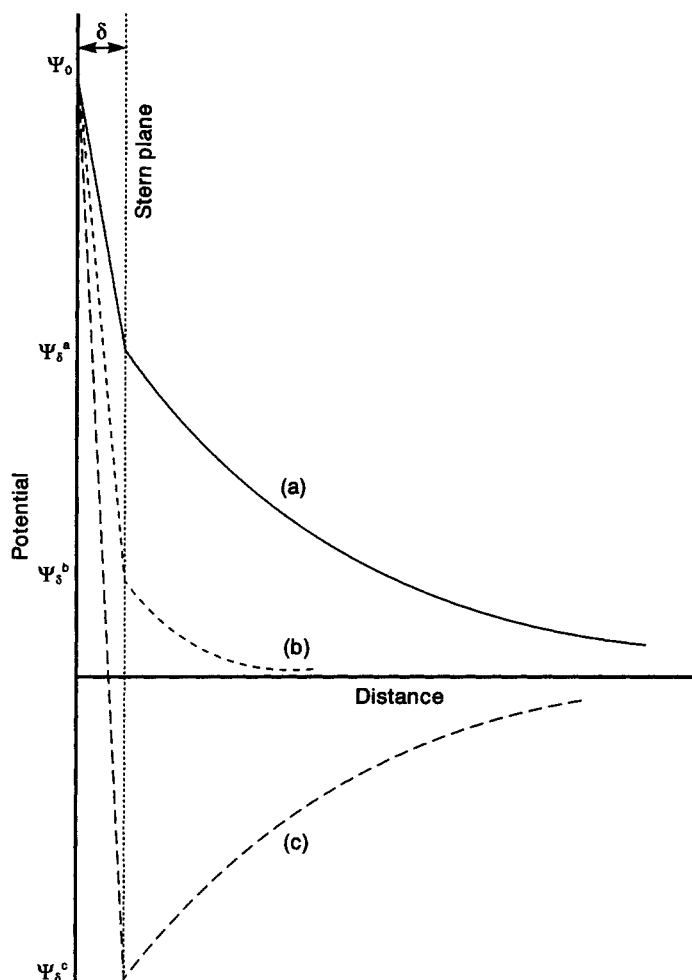
where  $N_s$  is the density of adsorption sites and  $x_i$  is the mole fraction of counterions in solution. The counterion valence  $z_i$  includes the sign of charge, so that the electrical interaction energy is negative (attraction), provided  $\psi_\delta$  is of opposite sign.

The presence of ‘fixed’ charge in the Stern layer means that it is no longer possible to equate the surface and diffuse layer charges. Instead we have:

$$\sigma_0 + \sigma_\delta + \sigma_1 = 0 \quad (2.21)$$

where  $\sigma_1$  is the diffuse layer charge per unit area of surface.

If the specific adsorption potential is large and favourable (i.e. negative), adsorption of counterions can continue until the Stern layer charge more than



**Figure 2.2** The variation of potential close to a charged interface: (a) in the case of a low concentration of indifferent electrolyte, (b) in the case of a higher concentration of indifferent electrolyte and (c) in the presence of a salt with specifically adsorbing counterions, giving charge reversal

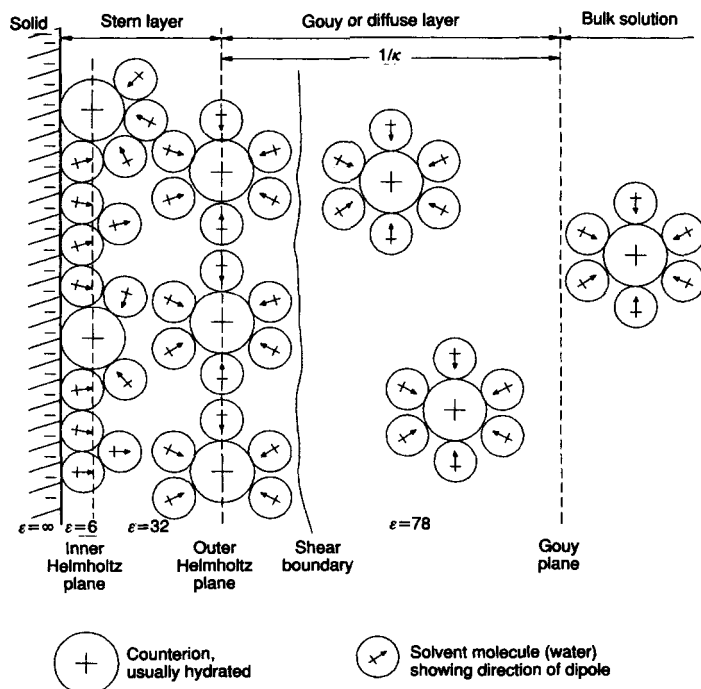
compensates the surface charge and *reversal of charge* occurs. This provides unequivocal evidence that some specific, non-electrical interaction is involved. Charge reversal can be brought about by many specifically adsorbing counterions, such as hydrolysing metal ions and polyelectrolytes, and is of great practical importance in particle aggregation and deposition.

Figure 2.2 shows schematically the effect of electrolytes on the distribution of potential in the double layer, for the case of an 'indifferent' electrolyte (i.e. with

no specifically adsorbing ions) at two concentrations, and a salt with a specifically adsorbing counterion, giving charge reversal.

## 2.2.4 The Stern–Grahame model

Although, for many purposes, the Stern model of the double layer is quite adequate, a number of further refinements can be made. One of these, due to Grahame (1947), subdivides the Stern layer into two regions: an inner layer occupied by specifically adsorbed, unhydrated ions (e.g. inner sphere complexes) and a second layer where hydrated counterions (outer sphere complexes) are located. The boundaries of these regions are often known as the *inner Helmholtz plane (IHP)* and *outer Helmholtz plane (OHP)*. The OHP is equivalent to the Stern plane. Outside this plane is the diffuse layer, adequately described by Gouy–Chapman theory.



**Figure 2.3** The Stern–Grahame model of the electrical double layer, showing the adsorption of unhydrated ions at the inner Helmholtz plane and of hydrated ions at the outer Helmholtz plane, together with a diffuse layer which extends outwards into the bulk solution. Likely values of the dielectric constant,  $\epsilon$ , are shown in the different regions. The electrokinetic shear boundary is thought to lie just outside the outer Helmholtz plane

One important feature of this model is that it admits the possibility of three different values of solvent permittivity. In aqueous systems the dielectric constant in the inner region will be quite low and is often assumed to be about 6 (representing dielectric saturation). In the outer region, where the field strength is rather lower, a value of about 30 might be appropriate. In the diffuse layer, the value for bulk water (78) is assumed. This approach has been quite often used, especially in the modelling of the oxide–water interface (Stumm, 1992), giving what are known as *triple layer models*.

A schematic diagram showing the essential features of the Gouy–Stern–Grahame double layer model is given in Figure 2.3.

## 2.2.5 Further refinements to the model

It has been recognized for some time (see, for example Hunter (1981)) that there is a fundamental inconsistency inherent in the Poisson–Boltzmann approach and a similar problem arises in the Debye–Hückel theory of electrolytes (Robinson and Stokes, 1965). The basic difficulty is that the expression for charge density, eqn (2.5), violates the electrostatic principle of linear superposition, since it does not predict that the potential at any point due to a collection of charged species will be the sum of potentials due to the individual charges. The expected linear dependence is only found for the low-potential approximation, which leads to eqn (2.11). The problem lies in the fact that the potential used in the Boltzmann expression, eqn (2.4), should be the *potential of mean force*, rather than the mean (time-averaged) potential. The former is calculated from the work required to bring the ion from bulk solution up to a particular point, a process which may involve some redistribution of charge.

This inconsistency has prompted a number of alternative, statistical-mechanical approaches (Buff and Stillinger, 1963; Martynov, 1966; Henderson *et al.*, 1983). The arguments between supporters of the Poisson–Boltzmann approach and its alternatives still continue, although their impact on practical aspects of colloid science has not been of great significance. This is partly due to the fact that electrical effects are less important in concentrated electrolyte solutions (where deviations from the Poisson–Boltzmann equation become more serious). In reality, the difficulties of implementing the alternative models under practical conditions (e.g. involving surface roughness) are too great.

Another noteworthy approach to this problem has involved the use of computer simulation. For instance, Torrie and Valleau (1979, 1980, 1982) have performed extensive Monte Carlo simulations of the double layer using a *primitive* model in which the electrolyte is considered to be an assembly of charged ‘hard spheres’ in a uniform dielectric medium. Their results show very good agreement with the Gouy–Stern–Grahame theory for the case where there is no specific adsorption and for relatively dilute electrolyte solutions ( $<0.1$  M).

In practice, there is probably little error involved in the use of the Poisson–Boltzmann expression, eqn (2.6), and this approach is adopted in nearly all cases.

## 2.2.6 Spherical double layers

So far, only planar interfaces have been considered and in this case the Poisson–Boltzmann equation can be solved analytically. However, for spherical particles an analytical solution is only possible for the low-potential (linear approximation) case.

The Poisson–Boltzmann equation for  $z$ - $z$  electrolytes, eqn (2.6), transposed into polar coordinates becomes:

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d\psi}{dr} \right) = \frac{2ze n_0}{\epsilon} \sinh \left( \frac{ze\psi}{kT} \right) \quad (2.22)$$

where  $r$  is the radial distance from the centre of the sphere.

For low potentials, such that  $\sinh y \approx y$ , the solution is simply:

$$\psi = \frac{\psi_0 a}{r} \exp [-\kappa(r - a)] \quad (2.23)$$

where  $a$  is the radius of the sphere and  $\psi_0$  is the surface potential.

(Strictly, eqn (2.23) applies only to a diffuse double layer. In the case of a Stern layer around the particle,  $\psi_0$  can be replaced by the Stern potential,  $\psi_s$ .)

It can be shown, by considering the total counterion charge, that the charge on a sphere is given by:

$$Q = 4\pi\epsilon\psi_0 a(1 + \kappa a) \quad (2.24)$$

The surface charge density follows immediately from this expression:

$$\sigma_0 = \frac{\epsilon\psi_0}{a} (1 + \kappa a) \quad (2.25)$$

As might be expected, in the case of diffuse layers which are thin compared to the particle radius (i.e.  $\kappa a \gg 1$ ), eqns (2.23) and (2.25) reduce to the corresponding flat plate expressions, eqns (2.11) and (2.17).

Because of the linear approximation, these expressions will become inaccurate for surface (or Stern) potentials greater than a few tens of millivolts in 1–1 electrolytes. In many cases of interest in particle aggregation and deposition, we are concerned with fairly low potentials and this restriction is not serious. Exact, numerical approaches to the problem of spherical double layers have been reviewed by Hunter (1981), together with some useful approximations for higher potentials. These will not be considered further here.

## 2.3 Electrokinetic phenomena

### 2.3.1 General

The most widely used experimental approach to the study of charged surfaces is through the use of electrokinetic techniques. Electrokinetic phenomena arise whenever there is relative movement between a charged interface and the adjacent electrolyte solution, so that part of the double layer charge moves with the liquid. Fundamental to these phenomena is the concept of a plane of shear,

which separates the 'fixed' from the 'mobile' parts of the electrical double layer. The electrical potential at the shear plane is the *electrokinetic potential*, or, more usually, the *zeta potential*, after the symbol  $\zeta$ , which is conventionally used to denote this quantity.

It is usually assumed that the shear plane lies outside but fairly close to the Stern plane (see Figure 2.3), so that essentially all of the diffuse layer charge is 'mobile' and the counterions in the Stern layer are 'fixed'. This means that values of 'surface charge' determined by electrokinetic techniques can be considerably less than the 'true' surface charge, measured by a titration method. Another important difference is between the PZC, obtained from a titration technique (see Section 2.2.1), and the *isoelectric point (IEP)*, which is the condition (usually pH value) at which the zeta potential becomes zero (see, for example, Lyklema (1978)). These two points coincide only in cases where there is no specific adsorption of ions. Where specific adsorption of counterions occurs, these become part of the 'fixed' charge and the point of zero electrokinetic potential will occur under conditions where the surface potential,  $\psi_0$ , determined by the concentration of potential-determining ions, has a non-zero value.

The relationship between the measured zeta potential and double layer structure is still a subject of debate and the shear plane cannot be located with any certainty. However, electrokinetic measurements are still of immense practical importance in colloid science, since they give information, however imperfect, which is not obtainable in any other way. There is a clear correlation, for instance, between zeta potential and colloid stability in very many cases. Colloidal particles are generally found to be stable if the zeta potential exceeds a certain value and to coagulate at lower values. Similarly, deposition of particles on surfaces is very often controlled by the zeta potentials of particles and substrate. Use of zeta potentials in quantitative expressions for electrical interaction (see Section 3.2) may not be strictly justified, but there is usually no real alternative.

We now briefly consider the main electrokinetic techniques and their interpretation. The available methods are as follows:

- (a) a *streaming potential* is established when solution is forced to flow through a tube, or porous plug, of material which acquires charge in contact with the solution
- (b) a *sedimentation potential* arises when charged particles settle through a solution
- (c) *electro-osmosis* is the flow of liquid through a tube or porous plug under the influence of an applied electric field
- (d) *particle electrophoresis* is the movement of charged particles in an electric field

Of these, the most commonly used techniques are streaming potential (sometimes streaming *current* is measured) to determine the zeta potential of granular or fibrous materials, and particle electrophoresis, to derive information on colloidal particles. However, it is convenient to start with an analysis of electro-osmosis, which provides a basis for a discussion of the other techniques. A more detailed account can be found in Hunter (1981).

### 2.3.2 Electro-osmosis

It is easiest to consider a flat interface, although the treatment is also applicable to electro-osmosis in cylindrical tubes, provided that the tube radius,  $r$ , is very much larger than the double layer thickness (i.e.  $\kappa r \gg 1$ ). An electric field,  $E$ , is assumed to be applied in a direction parallel to the surface and an element of moving fluid at some distance from the charged interface is subject to both electrostatic and viscous forces. If the fluid element has a thickness  $dx$  and a charge density  $\rho$  and the fluid velocity changes by an amount  $dv$  across the element, then it follows that:

$$E\rho dx = \frac{d}{dx} \left( \mu \frac{dv}{dx} \right) dx = \mu \frac{d^2v}{dx^2} dx \quad (2.26)$$

Substituting for  $\rho$  from the linear version of the Poisson equation, eqn (2.3), gives:

$$-E\epsilon \frac{d^2\psi}{dx^2} = \mu \frac{d^2v}{dx^2} \quad (2.27)$$

where  $\epsilon$  and  $\mu$  are the (local) values of the permittivity and viscosity, respectively.

Integration of eqn (2.27) can be carried out easily if it is assumed: (a) that the fluid velocity is zero at a plane where the potential  $\psi = \zeta$  (i.e. the shear plane) and attains a constant value,  $v_{eo}$ , far from the interface, where both  $\psi$  and  $d\psi/dx = 0$ , and (b) that  $\epsilon$  and  $\mu$  are constant (i.e. have their bulk solution values) over this entire region. The latter condition is more likely to apply if the mobile charge is entirely within the diffuse part of the double layer, although no assumption about the detailed structure of the double layer is implied. Integrating eqn (2.27) twice gives a very simple result for the electro-osmotic velocity,  $v_{eo}$ :

$$v_{eo} = \frac{E\epsilon\zeta}{\mu} \quad (2.28)$$

For aqueous solutions, this expression should apply to electro-osmotic flow in tubes with diameter greater than a few micrometres. In such cases the fluid velocity only varies over a region very close to the tube wall and is constant over most of the tube width. It is thus possible to calculate the volume flow rate through the tube,  $Q$ , by electro-osmosis; it is simply  $\pi r^2 v_{eo}$ . The tube radius can be eliminated by introducing the current,  $i$ , which, by Ohm's law, can be written:

$$i = E\pi r^2 \lambda_0 \quad (2.29)$$

where  $\lambda_0$  is the specific conductivity of the electrolyte solution. This gives:

$$\frac{Q}{i} = \frac{\epsilon\zeta}{\mu\lambda_0} \quad (2.30)$$

Thus, measuring the flow rate of a solution through a capillary tube under the influence of an applied electric field should, in principle, allow the zeta potential of the tube wall to be derived. It is only necessary to measure the flow rate and

the electric current, and to have values of the conductivity, permittivity and viscosity of the solution.

The advantage of eliminating the tube dimension is that eqn (2.30) should then apply to porous media as well as tubes, which would provide a means of determining the zeta potential of granular and fibrous media. In practice, this approach is complicated by *surface conductance*. The accumulation of counterions close to a charged interface can lead to a higher current than expected from the bulk conductivity of the solution, especially at low salt concentrations. If the surface conductivity is  $\lambda_s$ , then the result for tube flow is:

$$\frac{Q}{i} = \frac{\epsilon\zeta}{\mu(\lambda_0 + 2\lambda_s/r)} \quad (2.31)$$

It is difficult to account for surface conductance in porous media, where the pore geometry is uncertain. One approach is to determine the effective conductivity of the solution in the porous medium, by measuring the resistance *in situ*, and this can give adequate results.

Electro-osmosis is not often employed as a practical means of deriving zeta potentials, but it has an important effect in particle electrophoresis (see Section 2.3.4). It may also be used in practice as a means of dewatering (Sunderland, 1987) and remediation of contaminated soil (Shapiro and Probstein, 1993).

### 2.3.3 Streaming potential

When a solution flows through a cylindrical tube, with a charged inner wall, then part of the double layer charge is carried with the flowing solution and establishes a *streaming current*,  $I_s$ . This causes an electrical potential difference between the ends of the tube, which is the *streaming potential*. At steady state the streaming potential causes a conduction current,  $I_C$ , which just balances the streaming current. When the double layer is very thin compared to the tube radius, so that most of the charge is close to the tube wall, it is not difficult to show, using Poiseuille's equation for laminar tube flow and the Poisson equation for the solution charge density, that the streaming current is given by:

$$I_s = - \frac{\epsilon\zeta}{\mu} \pi r^2 \Delta P \quad (2.32)$$

where  $\Delta P$  is the pressure difference between the ends of the tube.

The streaming potential,  $E_s$ , at steady state is sufficient to produce a conduction current which just balances  $I_s$  and hence depends on the resistance presented by the tube. In general, the resistance depends on the tube dimensions, the solution conductivity,  $\lambda_0$ , and the surface conductivity,  $\lambda_s$ . The result is:

$$\frac{E_s}{\Delta P} = \frac{\epsilon\zeta}{\mu(\lambda_0 + 2\lambda_s/r)} \quad (2.33)$$

The similarity between this expression and eqn (2.31) for electro-osmotic flow is noteworthy. Comparison of the two shows that:

$$\left( \frac{E_s}{\Delta P} \right)_{i=0} = \left( \frac{Q}{i} \right)_{\Delta p=0} \quad (2.34)$$

This fundamental result is a direct consequence of the Onsager reciprocity principle in non-equilibrium thermodynamics.

If the surface conductance is negligible, then eqn (2.33) can be applied to porous media, since there is then no term for the dimensions of the tube. Measuring the streaming potential as a function of applied pressure should give a linear relationship and the zeta potential can be calculated from the slope. Where surface conductance is significant (as is often the case), the procedure becomes more complicated, although the measurement of the *in situ* conductivity, as in the case of electro-osmosis, can give satisfactory results.

To avoid problems of surface conductance, it is possible to measure the streaming current,  $I_s$ , directly and there are commercial devices available for this purpose (Dentel and Kingery, 1989). However, for studies of particle deposition on granular media, the zeta potential of the grains is usually determined by a streaming potential technique.

### 2.3.4 Particle electrophoresis

This is the most widely used electrokinetic technique and has very often been applied in studies of aggregation and deposition phenomena. In its simplest form, the motion of particles in an electric field is observed microscopically and the velocity is determined. The *electrophoretic mobility*,  $U$ , is defined as the velocity per unit field strength.

In practice electrophoretic mobilities are measured in either cylindrical or rectangular cells and modern instruments use laser Doppler techniques to derive the velocity, rather than direct microscopic observation. There is a practical problem caused by electro-osmotic flow at the cell walls. In a closed cell this results in a return flow through the centre of the cell and a characteristic velocity profile through the depth of the cell. Since the liquid flow is superimposed on the electrophoretic movement of the particles, the observed particle velocity is the sum of two terms. Provided that the liquid velocity is known, then it is, in principle, possible to calculate the true electrophoretic velocity. The more usual approach is to conduct the measurements at the *stationary levels*, where the liquid velocity is zero (the electro-osmotic flow is just balanced by the return flow). In this way the electrophoretic velocity may be observed directly.

For particles large compared with the double layer thickness ( $\kappa a \gg 1$ ), the velocity can be derived in exactly the same way as the electro-osmotic velocity at a planar interface, eqn (2.28), since we are only concerned with the *relative* velocity between particle and liquid and it makes no difference whether one or the other is stationary. In this case the electrophoretic mobility has a very simple form, known as the *Smoluchowski equation*:

$$U = \frac{\epsilon \zeta}{\mu} \quad (2.35)$$

This expression applies to fairly large particles in electrolyte solutions which are not too dilute. For particles of  $1\text{ }\mu\text{m}$  diameter in a  $10\text{ mM}$  solution of 1-1 electrolyte,  $\kappa a$  is about 160 and eqn (2.35) could be used with very little error. In such cases, for aqueous solutions at  $25^\circ\text{C}$ , inserting numerical values gives the following result for the zeta potential:

$$\zeta\text{ (mV)} = 12.8U\text{ (}\mu\text{m s}^{-1}\text{/V cm}^{-1}\text{)} \quad (2.36)$$

where the units of  $\zeta$  and  $U$  indicated are those conventionally used.

At the other extreme, where particles are very much smaller than the double layer extent ( $\kappa a \ll 1$ ), a different approach can be used. The electric force on the particle ( $=QE$ , where  $Q$  is the particle charge and  $E$  the field strength) and the Stokes drag ( $=6\pi\mu a v$ , where  $v$  is the particle velocity) must exactly balance under steady-state conditions. The particle charge relevant to electrokinetics is given by eqn (2.24), with  $\psi_0$  replaced by  $\zeta$ , provided that the zeta potential is not too large. With the condition  $\kappa a \ll 1$ , this approach gives an expression known as the *Hückel equation*:

$$U = \frac{2\epsilon\zeta}{3\mu} \quad (2.37)$$

This differs from eqn (2.35) only by a factor of  $2/3$ . The Hückel equation is not usually applicable to particle electrophoresis, since the condition  $\kappa \ll 1$  is only satisfied for very small particles in dilute electrolyte solutions. For particles of  $10\text{ nm}$  diameter, the concentration of 1-1 electrolyte would have to be less than  $50\text{ }\mu\text{M}$ . The expression is more often applicable to electrophoresis of macromolecules, such as proteins (although, strictly, the result applies only to spherical particles).

For particles of colloidal size, in solutions of moderate ionic strength,  $\kappa a$  often takes intermediate values and neither the Smoluchowski nor Hückel equation is appropriate. In such cases corrections have to be applied, which are discussed in some detail by Hunter (1981). Essentially there are two types of correction:

- (a) An *electrophoretic retardation effect* arises from the opposite movement of charged particles and counterions in an electric field, and acts, together with frictional resistance, to reduce the mobility. The derivation of the Smoluchowski expression, eqn (2.35), assumes that the electro-osmotic flow is equal and opposite to the particle motion and does not consider the frictional resistance on the particle. Both electrophoretic retardation and frictional drag are correctly incorporated in the Hückel equation and this accounts for the  $2/3$  difference between the two expressions. However, for  $\kappa \ll 1$ , the electrophoretic retardation effect is small, since very little of the force is transmitted to the particle. In the general case both electrophoretic and frictional retardation have to be incorporated and the result can be expressed as a correction factor to be applied to the Hückel expression:

$$U = \frac{2\epsilon\zeta}{3\mu} f_1(\kappa a) \quad (2.38)$$

The function  $f_1(\kappa a)$  depends on the particle shape and for spherical particles the value shows a smooth transition from 1 to 1.5 as  $\kappa a$  varies from 0 to  $\infty$ .

- (b) A *relaxation effect* arises because the motion of a charged particle causes the diffuse layer to become distorted. As the particle moves, it is not possible for the ions in the diffuse layer to respond instantly and so they lag behind the particle, giving an asymmetrical charge distribution, which causes the particles to move more slowly. This effect depends on  $\kappa a$ , the zeta potential and the limiting conductances of the ions. Modern treatments (e.g. O'Brien and White, 1978) include the electrophoretic retardation effect and so should give a complete description of the variation of mobility with zeta potential, particle size and ionic strength. Full computation of electrophoretic mobility using the numerical approach of O'Brien and White (1978) is quite straightforward and there are also simple analytical approximations which are in error by no more than a few per cent (Hunter, 1981).

The most important consequence of the relaxation correction is that the mobility can go through a maximum as the zeta potential is increased. However, the maximum does not occur until the zeta potential reaches 100 mV or more and such values are not often encountered in practice, especially in studies of particle aggregation.

Because of the uncertainties in calculating zeta potentials, electrophoretic data are often quoted as mobilities, which are unambiguous experimental quantities.

A more recent development is the field of *electroacoustics* (Hunter, 1993). When a suspension is subjected to high-frequency sound waves, the particles vibrate at the same frequency. Because of the different relaxation times of particles and ions in the diffuse layer, the latter respond more quickly to the ultrasonic waves, giving a small dipole. The cumulative effect of many such dipoles gives a measurable electric field which is known as the *colloid vibration potential*. The magnitude of this potential is proportional to the electrophoretic mobility of the particles. This is very useful for concentrated suspensions, where conventional electrophoresis is difficult. For essentially the same reason, application of an alternating electric field to a suspension of charged particles generates sound waves and gives rise to the *electrokinetic sonic amplitude* or *ESA effect*.

### 2.3.5 Interpretation of zeta potentials

Much of the above discussion has been concerned with the problem of deriving electrokinetic (zeta) potentials from electrokinetic measurements. Even when a completely satisfactory method is available, leading to reliable values of zeta potential, there remains the problem of relating zeta potentials to double layer properties. Essentially, the question is that of the location of the shear plane separating the 'fixed' from the 'mobile' part of the double layer.

The relationship between the zeta potential and the Stern potential,  $\psi_s$ , is of great interest, but cannot be established with any certainty, since there is no independent, direct method of measuring  $\psi_s$ . There are several cases, notably with latex particles, where the measured zeta potential passes through a maximum as ionic strength is increased. Such behaviour is not expected for the Stern potential, which should decrease as the concentration of (indifferent) electrolyte is increased. Several explanations have been proposed to explain this anomaly, such as the 'hairy' nature of the polymer latex surface as a result of protruding polymer chains (van den Hoven and Bijsterbosch, 1987). In such cases the approach of counterions to the surface may be restricted and the plane of shear may be displaced outwards. Similar effects might be expected with adsorbed polymers. Another explanation is that there may be increasing adsorption of co-ions on hydrophobic areas of the latex surface as the salt concentration is increased (Elimelech and O'Melia, 1990). Since latex particles are very often used in model studies of aggregation and deposition, it is important to understand their electrokinetic behaviour.

In the case of oxide particles it is possible to derive the surface charge density by acid-base titration and there have been many attempts to relate these measurements with electrokinetic data determined under similar conditions. Generally, the surface charge determined by titration can be much greater than the 'electrokinetic charge,' implying that much of the counterion charge lies inside the plane of shear. Several models of the oxide-water interface have been developed, including triple layer models (Yates *et al.*, 1974; Davis and Leckie, 1978). However, in order to obtain good fits with experimental data, rather arbitrary choices of affinity constants of protons and other ions to surface sites have to be made. An alternative approach of Hiemstra and van Riemsdijk (1991), which recognizes that different faces of oxide crystals contribute to the surface charge in different ways, seems to provide a more rational explanation of observed behaviour.

From the standpoint of colloid stability, a very important point is the distance of the shear plane from the 'true' particle surface. In calculating the interaction between particles as a function of separation distance, it is usual to assume that the attractive, van der Waals forces operate between the particles and so the correct distance to use is the separation between the surfaces. However, if zeta potentials are used to calculate electrical interaction, it is the separation between shear planes which is appropriate. If the shear plane is located 0.5 nm from the particle surface, then, effectively, the electrical interaction between two particles operates over a distance 1 nm less than the van der Waals interaction. Since both interactions decrease strongly with separation distance (see Chapter 3), this effect can give a substantially increased particle stability (because of the greater influence of the electrical repulsion term). This point has been discussed by Duckworth and Lips (1978) and can significantly influence interpretation of colloid stability data (Penners and Koopal, 1987).

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