

Charged interfaces

The electric double layer

Most substances acquire a surface electric charge when brought into contact with a polar (e.g. aqueous) medium, possible charging mechanisms (elaborated below) being ionization, ion adsorption and ion dissolution. This surface charge influences the distribution of nearby ions in the polar medium. Ions of opposite charge (*counterions*) are attracted towards the surface and (less important) ions of like charge (*co-ions*) are repelled away from the surface. This, together with the mixing tendency of thermal motion, leads to the formation of an electric double layer made up of the charged surface and a neutralizing excess of counter-ions over co-ions distributed in a diffuse manner in the polar medium. The theory of the electric double layer deals with this distribution of ions and, hence, with the magnitude of the electric potentials which occur in the locality of the charged surface. This is a necessary first step towards understanding many of the experimental observations concerning the electrokinetic properties, stability, etc., of charged colloidal systems.

Origin of the charge at surfaces

Ionization

Proteins acquire their charge mainly through the ionizations of carboxyl and amino groups to give COO^- and NH_3^+ ions. The ionization of these groups, and so the net molecular charge, depends strongly on the pH of the solution. At low pH a protein molecule will be positively charged and at high pH it will be negatively charged. The pH at which the net charge (and electrophoretic mobility) is zero is called the *iso-electric point*.

Ion adsorption

A net surface charge can be acquired by the unequal adsorption of oppositely charged ions. Ion adsorption may involve positive or negative surface excess concentrations.

Surfaces in contact with aqueous media are more often negatively charged than positively charged. This is a consequence of the fact that cations are usually more hydrated than anions and so have the greater tendency to reside in the bulk aqueous medium; whereas the smaller, less hydrated and more polarizing anions have the greater tendency to be specifically adsorbed. Hydrocarbon oil droplets and even air bubbles suspended in water and in most aqueous electrolyte solutions have negative electrophoretic mobilities (i.e. they migrate towards the anode under the influence of an applied electric field)¹⁸⁰. This net negative charge is explained in terms of negative adsorption of ions. The addition of simple electrolytes, such as NaCl results in an increase in the surface tension of water (see Figure 11) and in the interfacial tension between hydrocarbon oil and water. This is interpreted via the Gibbs equation in terms of a negative surface excess ionic concentration. The surface excess concentrations of hydrogen and hydroxyl ions will also be negative. Presumably, cations move away from the air bubble-water and oil-water interfaces more than anions, leaving the kinetic units (which will include some aqueous medium close to the interfaces) with net negative charges.

Preferential negative adsorption of hydrogen ions compared with hydroxyl ions is reflected in the electrophoretic mobility-pH curve for hydrocarbon oil droplets (see Figure 7). The magnitude of the electrophoretic mobilities of inert particles such as hydrocarbon oil droplets (c 0 to $-6 \times 10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}$) is comparable with those of simple ions (e.g. $-7.8 \times 10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}$ for Cl ions at infinite dilution in aqueous solution at 25°C), which, in view of their relatively large size, reflects a high charge number.

Surfaces which are already charged (e.g. by ionization) usually show a preferential tendency to adsorb counter-ions, especially those with a high charge number. It is possible for counter-ion adsorption to cause a reversal of charge.

If surfactant ions are present, their adsorption will usually determine the surface charge.

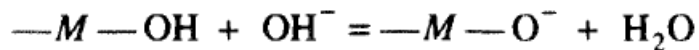
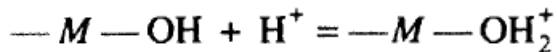
Hydrated (e.g. protein and polysaccharide) surfaces adsorb ions less readily than hydrophobic (e.g. lipid) surfaces.

Ion dissolution

Ionic substances can acquire a surface charge by virtue of unequal dissolution of the oppositely charged ions of which they are composed.

Silver iodide particles in aqueous suspension are in equilibrium with a saturated solution of which the solubility product, $a_{\text{Ag}^+} a_{\text{I}^-}$, is about 10^{-16} at room temperature. With excess I^- ions, the silver iodide particles are negatively charged; and with sufficient excess Ag^+ ions, they are positively charged. The zero point of charge is not at $\text{p Ag } 8$ but is displaced to $\text{p Ag } 5.5$ ($\text{p I } 0.5$), because the smaller and more mobile Ag^+ ions are held less strongly than the I^- ions in the silver iodide crystal lattice. The silver and iodide ions are referred to as *potential-determining* ions, since their concentrations determine the electric potential at the particle surface. Silver iodide sols have been used extensively for testing electric double layer and colloid stability theories.

In a similar way, hydrogen and hydroxyl ions are potential determining for hydrous metal oxide sols:



The surface electrochemistry of hydrous metal oxides is actually much more complicated than this, with a range of individual inorganic reactions possible, depending on factors such as surface crystal structure.

Adsorption and orientation of dipoles

Adsorption of dipolar molecules will not contribute to a net surface charge, but the presence of a layer of orientated dipolar molecules at the surface may make a significant contribution to the nature of the electric double layer.

The diffuse double layer

The electric double layer can be regarded as consisting of two regions: 'an inner region which may include adsorbed ions, and a diffuse region in which ions are distributed according to the influence of electrical forces and random thermal motion. The diffuse part of the double layer will be considered first.

Quantitative treatment of the electric double layer represents an extremely difficult and in some respects unresolved problem. The requirement of overall electroneutrality dictates that, for any dividing surface, if the charge per unit area is $+\sigma$ on one side of the surface, it must be $-\sigma$ on the other side. It follows, therefore, that the magnitude of σ will depend on the location of the surface. Surface location is not a straightforward matter owing to the geometric and chemical heterogeneity which generally exists. It follows, furthermore, that electric double-layer parameters (potentials, surface charge densities, distances) are not amenable to unequivocal definition. Despite this, however, various simplifications and approximations can be made which allow double-layer theory to be developed to a high level of sophistication and usefulness.

The simplest quantitative treatment of the diffuse part of the double layer is that due to Gouy (1910) and Chapman (1913), which is based on the following model:

1. The surface is assumed to be flat, of infinite extent and uniformly charged.
2. The ions in the diffuse part of the double layer are assumed to be point charges distributed according to the Boltzmann distribution.
3. The solvent is assumed to influence the double layer only through its dielectric constant, which is assumed to have the same value throughout the diffuse part.
4. A single symmetrical electrolyte of charge number z will be assumed. This assumption facilitates the derivation while losing little owing to the relative unimportance of co-ion charge number.

Let the electric potential be ψ_0 at a flat surface and ψ at a distance x from the surface in the electrolyte solution. Taking the surface to be positively charged (Figure 7.1) and applying the Boltzmann distribution

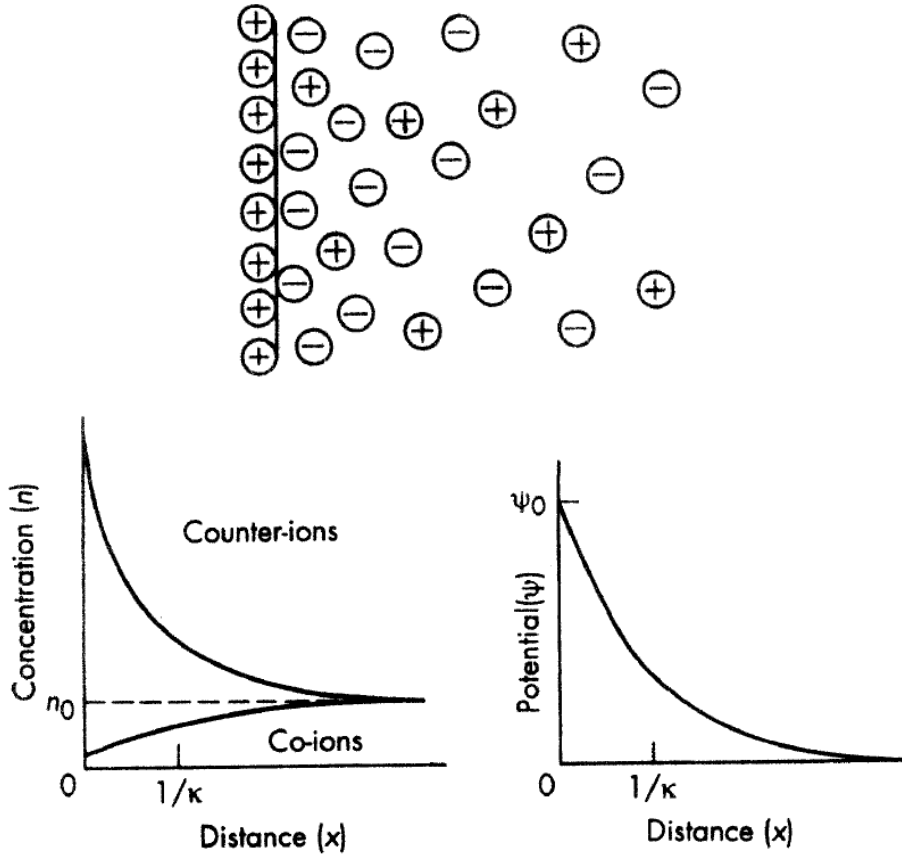


Figure 7.1 Schematic representation of a diffuse electric double layer

$$n_+ = n_0 \exp\left[\frac{-ze\psi}{kT}\right] \quad \text{and} \quad n_- = n_0 \exp\left[\frac{+ze\psi}{kT}\right]$$

where n_+ and n_- are the respective numbers of positive and negative ions per unit volume at points where the potential is ψ (i.e. where the electric potential energy is $ze\psi$ and $-ze\psi$ respectively), and n_0 is the corresponding bulk concentration of each ionic species. The net volume charge density ρ at points where the potential is ψ is, therefore, given by

$$\begin{aligned} \rho &= ze(n_+ - n_-) \\ &= zen_0 \left(\exp\left[\frac{-ze\psi}{kT}\right] - \exp\left[\frac{+ze\psi}{kT}\right] \right) \\ &= -2zen_0 \sinh \frac{ze\psi}{kT} \end{aligned} \tag{1}$$

ρ is related to ψ by Poisson's equation, which for a flat double layer takes the form

$$\frac{d^2 \psi}{dx^2} = -\frac{\rho}{\epsilon} \quad (2)$$

where ϵ is the permittivity*.

Combination of equations (7.1) and (7.2) gives

$$\frac{d^2 \psi}{dx^2} = \frac{2ze n_0}{\epsilon} \sinh \frac{ze\psi}{kT} \quad (3)$$

The solution⁸⁷ of this expression, with the boundary conditions ($\psi = \psi_0$ when $x = 0$; and $\psi = 0, d\psi/dx = 0$ when $x = \infty$) taken into account, can be written in the form

$$\psi = \frac{2kT}{ze} \ln \left(\frac{1 + \gamma \exp[-\kappa x]}{1 - \gamma \exp[-\kappa x]} \right) \quad (4)$$

where

$$\gamma = \frac{\exp[ze\psi_0 / 2kT] - 1}{\exp[ze\psi_0 / 2kT] + 1} \quad (5)$$

and

$$\kappa = \left(\frac{2e^2 n_0 z^2}{\epsilon kT} \right)^{1/2} = \left(\frac{2e^2 N_A c z^2}{\epsilon kT} \right)^{1/2} = \left(\frac{2F^2 c z^2}{\epsilon RT} \right)^{1/2} \quad (6)$$

$$\text{Or } \frac{1}{\kappa} = \left(\frac{\epsilon_0 \epsilon K T}{10^3 e^2 \sum_i c_i z_i^2 N_A} \right)^{1/2}$$

Where c is the concentration mol dm^{-3} , ϵ_0 is permittivity of vacuum ($\text{C}^2 \text{N}^{-1} \text{m}^{-1}$) and ϵ is dielectric constant dimensionless, κ again is ionic thickness

where N_A is Avogadro's constant and c is the concentration of electrolyte.

If $ze\psi_0/2kT \ll 1$ ($kT/e = 25.6 \text{ mV}$ at 25°C), the Debye-Hückel approximation,

$$\left(\exp \left[\frac{ze\psi_0}{2kT} \right] \approx 1 + \frac{ze\psi_0}{2kT} \right)$$

can be made and equations (4) and (5) simplify to

$$\psi = \psi_0 \exp[-\kappa x] \quad (7)$$

which shows that at low potentials the potential decreases exponentially with distance from the charged surface. Close to the charged surface, where the potential is likely to be

relatively high and the Debye-Hückel approximation inapplicable, the potential is predicted to decrease at a greater than exponential rate.

The potential ψ_o can be related to the charge density σ_o at the surface by equating the surface charge with the net space charge in

the diffuse part of the double layer (i.e. $\sigma_o = - \int_0^\infty \rho dx$) and applying

the Poisson-Boltzmann distribution. The resulting expression is

$$\sigma_o = (8n_0\epsilon kT)^{1/2} \sinh \frac{ze\psi_o}{2kT} \quad (8)$$

which at low potentials reduces to

$$\sigma_o = \epsilon\kappa\psi_o \quad (9)$$

The surface potential σ_o , therefore, depends on both the surface charge density ψ_o and (through κ) on the ionic composition of the medium. If the double layer is compressed (i.e. κ increased), then either ψ_o must increase, or ψ_o must decrease, or both.

In many colloidal systems, the double layer is created by the adsorption of potential-determining ions; for example, the potential ψ_o at the surface of a silver iodide particle depends on the concentration of silver (and iodide) ions in solution. Addition of inert electrolyte increases κ and results in a corresponding increase of surface charge density caused by the adsorption of sufficient potential-determining silver (or iodide) ions to keep ψ_o approximately constant. In contrast, however, the charge density at an ionogenic surface remains constant on addition of inert electrolyte (provided that the extent of ionization is unaffected) and ψ_o decreases.

From equation (9) it can be seen that, at low potentials, a diffuse double layer has the same capacity as a parallel plate condenser with a distance $1/\kappa$ between the plates. It is customary to refer to $1/\kappa$ (the distance over which the potential decreases by an exponential factor at low potentials) as the 'thickness' of the diffuse double layer. For an aqueous solution of a symmetrical electrolyte at 25°C, equation (6) becomes

$$\kappa = 0.329 \times 10^{10} \left(\frac{cz^2}{\text{mol dm}^{-3}} \right)^{1/2} \text{m}^{-1} \quad (10)$$

For a 1-1 electrolyte the double layer thickness is, therefore, about 1 nm for a $10^{-1} \text{ mol dm}^{-3}$ solution and about 10 nm for a $10^{-2} \text{ mol dm}^{-3}$ solution. For unsymmetrical electrolytes the double layer thickness can be calculated by taking z to be the counter-ion charge number.

The Poisson-Boltzmann distribution for a spherical interface takes the form

$$\nabla^2 \psi = \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\psi}{dr} \right) = \frac{2zen_0}{\epsilon} \sinh \frac{ze\psi}{kT} \quad (11)$$

where r is the distance from the centre of the sphere. This expression cannot be integrated analytically without approximation to the exponential terms. If the Debye-Hückel approximation is made, the equation reduces to

$$\nabla^2 \psi = \kappa^2 \psi \quad (12)$$

which, on integration (with the boundary conditions, $\psi = \psi_0$ at $r = a$ and $\psi = 0$, $d\psi/dr = 0$ at $r = \infty$, taken into account) gives

$$\psi = \psi_0 \frac{a}{r} \exp[-\kappa(r - a)] \quad (13)$$

Unfortunately, the Debye-Hückel approximation ($z\psi \ll c.25mV$) is often not a good one in the treatment of colloid and surface phenomena. Unapproximated, numerical solutions of equation (11) have been computed