the more recent introduction of polymers now provides a wide variety of membrane types. Natural membranes are essential components in all biological systems: they form the containers that retain the contents of animal and plant cells, and control the movement of various molecules, from oxygen and carbon dioxide to food and waste materials, from one part of the organism to another. They are discussed at greater length in Section 10.5.

The essential feature of both artificial and natural membranes is their selective permeability. Their function is not simply to separate two bulk liquid phases, but to permit the transport of selected materials from one liquid to the other while preventing the passage of others. In early work on colloids the term *semipermeable membrane* was used to describe membranes that would allow the passage of simple inorganic ions and solvent molecules while preventing the larger particles of colloidal dispersions from passing through.

The present discussion will be divided into three parts, dealing with *artificial membranes, black lipid membranes*, and with *self-assembled membranes*. By artificial membranes we mean membranes that have been introduced artificially to the system, even though they may have been formed elsewhere by some natural process: pig bladder, for instance. In contrast, the self-assembled membranes form spontaneously from components of the system, often amphiphiles. Black lipid membranes are essentially artificial membranes, but they are so different from other artificial membranes that they need to be treated separately.

6.7.1 Artificial membranes

Osmotic pressure

The ability of a semipermeable membrane to exhibit selectivity in the passage of molecules is clearly demonstrated by the phenomenon of osmosis. If, for example, an aqueous solution of sucrose is placed in an inverted thistle funnel with the wide end tightly covered by cellophane, and this end is immersed in water, water will flow through the cellophane, but sucrose is unable to pass through, so the liquid level in the tubular part of the funnel rises (Figure 6.5). This process will continue until equilibrium is reached.

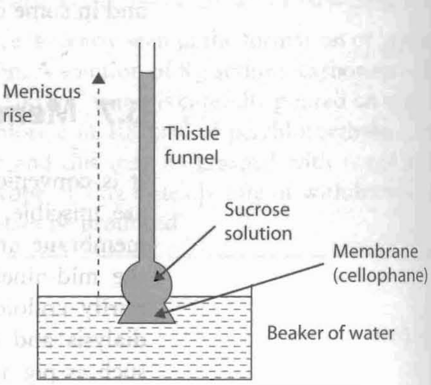

Figure 6.5. Apparatus for demonstrating osmotic flow.

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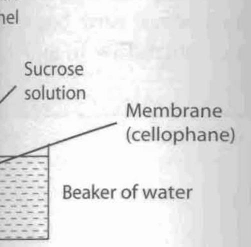

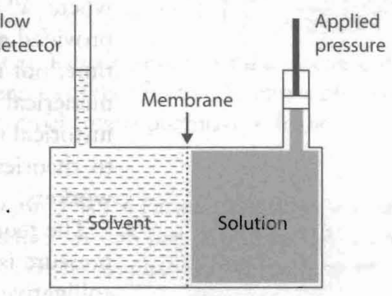

Figure 6.6. Schematic diagram of apparatus for the measurement of osmotic pressure. The osmotic pressure is the pressure that must be exerted on the solution that is just sufficient to prevent movement of solvent through the membrane into the solution.

At equilibrium, the pressure exerted by the movement of solvent into the funnel is exactly balanced by the hydrostatic pressure from the column of liquid in the funnel. This pressure is the **osmotic pressure**. The apparatus shown in Figure 6.5, while useful as a demonstration of osmosis, is not satisfactory for measuring osmotic pressure as the concentration of the solution in the funnel changes as the osmotic flow proceeds and the solute concentration is probably not uniform.

Osmotic pressure is defined as the pressure just required to prevent osmotic flow, and in its measurement the extent of osmotic flow must be minimized. A suitable design is shown schematically in Figure 6.6.

The analysis of this experiment is treated in most physical chemistry texts so will be only briefly outlined here. At equilibrium the change in free energy caused by the presence of solute must be balanced by the change coming from the increased pressure (the osmotic pressure, Π^{os}).

For the effect of solute (B) on the vapour pressure of solvent (A),

$$\Delta G = n_A RT \ln(p/p^\bullet)$$

and for the pressure increase,

$$\Delta G = V\Pi^{\mathrm{os}}$$

so that at equilibrium,

$$n_A RT \ln(p/p^\bullet) + V\Pi^{\mathrm{os}} = 0. \qquad (6.11)$$

If the solution is dilute we can assume Raoult's law for the solvent,

$$p/p^\bullet = x_A = 1 - x_B$$

and use the approximation

$$\ln(1 - x_B) \approx -x_B$$

giving

$$\Pi^{\mathrm{os}} V/n_A = RTx_B \qquad (6.12)$$

where V/n_A is the molar volume of *solvent*. With some further approximations Eq. (6.12) can be changed into the empirical equation devised by van't Hoff in 1885:

$$\Pi^{\mathrm{os}} V' = n_B RT \qquad (6.13)$$

where V' is the volume of solution rather than solvent. This equation provided a reasonable fit to much of the experimental data available to that time, but there was one important anomaly: when the solute was ionised a numerical factor, the van't Hoff *i* factor, had to be inserted. It is a matter of historical record that these *i* factors provided significant experimental support to theories of ionization developed at about 1887 by Arrhenius and later workers.

The requirement to insert the van't Hoff factor into equations for osmotic pressure is a consequence of the colligative nature of osmotic pressure: with colligative properties the value depends on the total concentration of solute particles and not on the nature of these particles. Thus when, for example, surfactant molecules aggregate to form micelles the dependence of osmotic pressure on total surfactant concentration changes markedly, as shown in Figure 4.15.

Dialysis

Semipermeable membranes are frequently used to purify colloidal dispersions, sols or emulsions. Here the membrane must be able to allow small ions to pass through as well as solvent molecules while retaining the colloid particles. Cellophane (a reprecipitated cellulose) is commonly used. For purification purposes the cellophane comes as a tube that can be cut and tied to form a bag. Boiling in several changes of distilled water to remove soluble impurities (introduced to prevent embrittlement) is usually desirable before use. The impure colloid is sealed in the bag and immersed in distilled water which is changed several times over a period of days. Ions present in the colloid as impurities will diffuse out of the bag, driven by the concentration difference, while water will tend to enter the bag by osmosis. It is therefore important that the bag should be strong enough to withstand the osmotic pressure that will develop.

Donnan membrane equilibrium

If a dispersion of large charged molecules such as a protein is placed on one side of a semipermeable membrane and solvent or a solution of a simple electrolyte on the other, there will be a redistribution of ions. In the situation illustrated in Figure 6.7, the large P^- ions are unable to pass through the membrane, but the Na^+ and Cl^- ions can. We end up with an asymmetric distribution of the small ions, the *Donnan effect*, and an electrical potential across the membrane.

Initially there are no Cl^- ions in solution α, so there is a net movement of Cl^- from β. To preserve electrical neutrality, this movement must be accompanied by the movement of an equal number of Na^+ ions from β to α. This process continues until the activity products, $a(Na^+) \cdot a(Cl^-)$, are the same on both sides of the membrane. This generates a difference in electrical potential across the membrane: the Donnan potential. Further treatment of this system requires an understanding of electrochemical potentials ($\overline{\mu}_i$) which are described below.

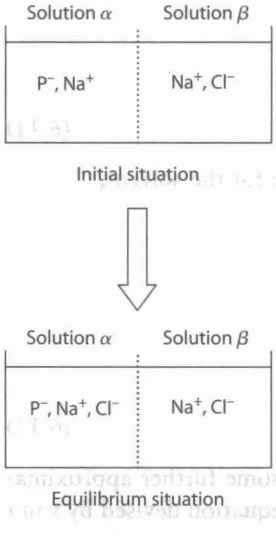

Figure 6.7. The movement of ions in the Donnan membrane equilibration process.

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Electrochemical potential

In dealing with the movement of ions as distinct from neutral molecules, it is necessary to modify the chemical potentials of the ions to take into account the electrostatic free energy. Thus the electrochemical potential is defined as

$$\bar{\mu}_i = \mu_i + z_i F\Phi \tag{6.14}$$

where z_i is the charge number of the i ion, F is the Faraday constant, and Φ is the electrostatic potential. Assuming that we can use concentrations rather than activities in the expression for free energy, we have for the movement of i from phase α to phase β:

$$\begin{aligned}\bar{\mu}_i^\beta - \bar{\mu}_i^\alpha &= \mu_i^\beta - \mu_i^\alpha + z_i F(\Phi^\beta - \Phi^\alpha)\\ &= RT\ln\left(\frac{c_i^\beta}{c_i^\alpha}\right) + z_i F(\Phi^\beta - \Phi^\alpha).\end{aligned} \tag{6.15}$$

At equilibrium the electrochemical potentials must be equal.

At the Donnan equilibrium

$$\bar{\mu}_{\mathrm{Na}}^\beta - \bar{\mu}_{\mathrm{Na}}^\alpha = 0 = \bar{\mu}_{\mathrm{Cl}}^\beta - \bar{\mu}_{\mathrm{Cl}}^\alpha$$

and the potential difference across the membrane must be the same for both the Na$^+$ and Cl$^-$ ions, so that:

$$\Phi^\beta - \Phi^\alpha = -\frac{RT}{z_{\mathrm{Na}}F}\ln\left(\frac{c_{\mathrm{Na}}^\beta}{c_{\mathrm{Na}}^\alpha}\right) = -\frac{RT}{z_{\mathrm{Cl}}F}\ln\left(\frac{c_{\mathrm{Cl}}^\beta}{c_{\mathrm{Cl}}^\alpha}\right). \tag{6.16}$$

Furthermore, as $z_{\mathrm{Na}} = -z_{\mathrm{Cl}}$

$$\frac{c_{\mathrm{Na}}^\beta}{c_{\mathrm{Na}}^\alpha} = \frac{c_{\mathrm{Cl}}^\alpha}{c_{\mathrm{Cl}}^\beta}$$

whence

$$c_{\mathrm{Na}}^\beta c_{\mathrm{Cl}}^\beta = c_{\mathrm{Na}}^\alpha c_{\mathrm{Cl}}^\alpha. \tag{6.17}$$

This relationship, with activities replaced by concentrations, confirms the statement made earlier about the equilibrium situation.

The condition of electrical neutrality for each solution requires that

$$c_{\mathrm{Na}}^\beta = c_{\mathrm{Cl}}^\beta = c^\beta$$

and

$$c_{\mathrm{Na}}^\alpha = c_{\mathrm{Cl}}^\alpha - z_{\mathrm{P}}c_{\mathrm{P}}^\alpha$$

(noting that z_{P} is negative). Substituting these two equations into (6.17) gives a quadratic which yields the approximate solution:

$$\left(\frac{c_{\mathrm{Na}}^\alpha}{c_{\mathrm{Na}}^\beta}\right) = 1 - \frac{z_{\mathrm{P}}c_{\mathrm{P}}^\alpha}{2c_{\mathrm{Na}}^\beta} \tag{6.18}$$

From this relationship and (6.16) the Donnan potential $(\Phi^\beta - \Phi^\alpha)$ can be calculated from the characteristics of the polymer and the concentration of Na$^+$ in the external solution.

Generally there would be a tendency for water to flow by osmosis from solution β to solution α. The osmotic pressure applied to solution α to prevent this flow would contribute an additional term to the definition of electrochemical potential, but this term is usually small and has been neglected in the above treatment.

6.7.2 Black lipid membranes (BLMs)

A wide range of amphiphiles may be used to form black lipid membranes between two aqueous solutions. The two amphiphile monolayers are arranged with their hydrophilic groups facing out towards the aqueous solutions, and their hydrophobic portions towards one another, usually with an oil layer between them. Typically the area of a BLM is quite small (<1 mm diameter).

A BLM may be formed by placing a drop of solution containing the amphiphile in a small hole in a partition separating two aqueous solutions. Another method is a variation of the Langmuir–Blodgett technique for depositing monolayers on solid substrates. In this case the substrate has a small hole in it and the monolayer bridges over the hole on both sides as the substrate is immersed. After initial formation a BLM formed with solvent will begin to thin (draining up or down depending on the relative densities of solvent and aqueous solution) and eventually show interference colours and ultimately black spots which merge to cover the entire film.

Fundamental to most studies involving a BLM is knowledge of its thickness. This is usually determined by an optical reflectance technique with the data modelled by a single- or a triple-layer (two surfactant layers and the solvent core) model.

One of the main objectives in studying BLMs is to mimic biological membranes. This usually requires the addition of non-lipid materials either during BLM formation or after formation. Transport and electrical phenomena are of major biological interest and will be discussed further in Chapter 10.

For a review of this topic see H.Ti. Tien (1988).

6.7.3 Self-assembled membranes

We have already seen that amphiphiles in solution can associate to form micelles, but other structures are also possible. Micelles can be spherical, tubular or sausage shaped, lamellar, or inverted. Bilayer structures can be simple sheets, or curved into more or less spherical closed structures known as liposomes or vesicles. Furthermore, there can be several stacked bilayers in these various configurations. Finally, bicontinuous structures can be formed. Generally within these various structures the hydrophobic parts of the amphiphiles are fluid-like, rather than solid, with vigorous thermal motion within the aggregate.

The forces involved in forming a particular aggregate comprise the attractive/repulsive forces between amphiphile molecules, the interaction