

CHAPTER II

THEORETICAL BACKGROUND

When an ion-exchange reaction is carried out by a "batch" method—that is, by putting a quantity of an ion exchanger such as resin into a certain volume of solution—the reaction begins at once, but a certain time elapses before the equilibrium state is reached. It is generally a simple matter to determine the rate of exchange, for example, by sampling and analysing the solution at intervals or by making use of some physical properties which change as the reaction proceeds.

Equilibrium between ion exchangers and solutions can be described by means of rigorous thermodynamics. This treatment is quite general and requires in principle no model and no assumptions about the mechanical or microscopic images which would lead us to a feeling of greater understanding of the phenomena.

Equilibrium with solvent

Ion exchangers are able to absorb the solvent in which they are placed. This absorption is accompanied by the development of swelling pressure within the exchanger phase. The first solvent molecules entering the exchanger solvate the ionic groups within the matrix and as it proceeds the randomly arranged polymer chains unfold

to allow for the greater bulk of the solvated ions. Counter ions and fixed ionic groups then constitute a very concentrated internal ionic solution. Consequently, as with any concentrated solution in contact with pure solvent, there is a tendency for ions to diffuse out of the exchanger and into the bathing solvent. Since one species of charge is fixed, only counter ions may freely diffuse. At the same time, external solvent molecules tend to be driven into the exchanger in an attempt to reduce the high concentration of the internal ionic solution of the ion exchanger phase. Dissolution of the exchanger is prevented by its cross-linking, but swelling remains as a result of the difference in concentration between the ion exchanger and external solutions. This swelling pressure is the balancing force between the opposing tendencies of dilution of the internal solution and the rigidity of the exchanger matrix which tends to prevent such dilution. The situation is one analogous to osmotic equilibrium. On the basis of this simple model a number of phenomena are rationalised i.e.,

(a) That polar solvents are, in general, better swelling agents than non-polar ones, due to their greater ability to solvate ions.

(b) That swelling is reduced in highly cross-linked polymers, due to increased rigidity (although the swelling pressure is higher).

(c) That swelling increases with capacity, particularly when the ionic components of the exchanger are known to show no serious tendency to ion pairing or complexing.

(d) That, for a given exchanger, swelling is reduced when the concentration of the external electrolyte is increased.

The origin and concept of the Donnan membrane potential⁽⁴⁾

First, the origin of the electrostatic force in the system will be studied. Suppose that a cation exchanger (containing no sorbed electrolyte) is placed in a dilute solution of a strong electrolyte. There are considerable concentration differences between the two phases; the cation concentration is larger in the ion exchanger, whereas the (mobile) anion concentration is larger in the solution. If the ions carried no electric charges, these concentration differences would be levelled out by diffusion. However, such a process would disturb electroneutrality since, actually, the ions are charged. Migration both of cations into the solution and of anions into the ion exchanger results in an accumulation of positive charge in the solution and of negative charge in the ion exchanger. In this process, each counter ion which does leave the exchanger phase leaves behind an uncompensated charge on the matrix of the exchanger, making it more difficult to remove further counter ions, which now must do an increased amount of electrical work in escaping. Those which do diffuse out into the solvent remain near to the surface of the exchanger in a diffuse double layer. The separation of charge involved in this process set up an electrical potential across the exchanger-solution interface: the Donnan membrane potential. This is illustrated diagrammatically in Figure 2.1. It must be stressed that very few ions indeed are sufficient to set up quite substantial voltages and also that the developed potential tends to return the counter ions of the double layer to their

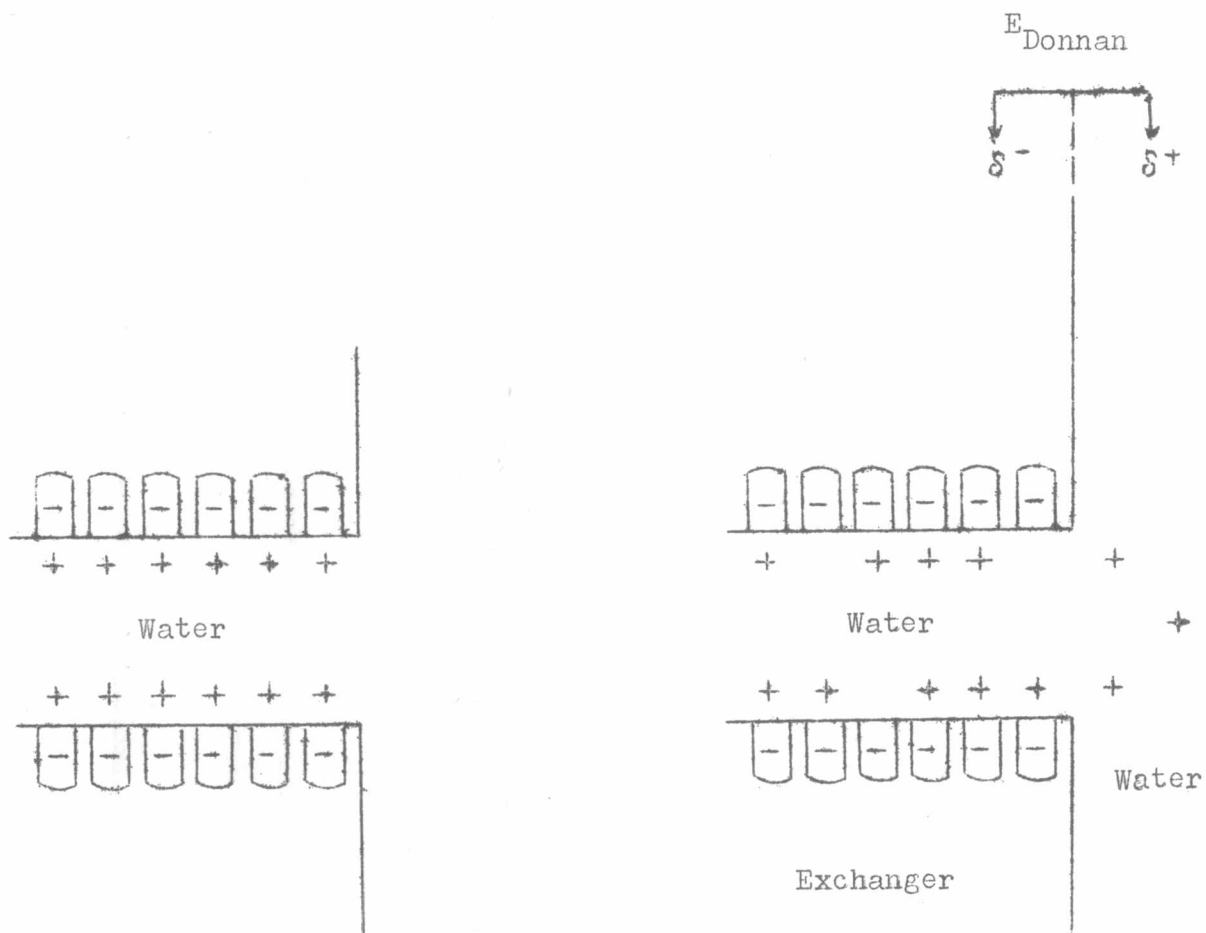


Fig. 2-1 The development of a Donnan potential at an exchanger/solution interface. Left: A hypothetical pore of a cation exchanger before immersion. Right: After immersion in water solvent.

matrix sites. The ions of the double layer are never a significant fraction of the exchanger capacity and so electroneutrality within the exchanger phase may be considered to be exactly maintained.

These very few ions and the resulting potential developed in their removal are of the utmost importance in our understanding of all ion exchange processes. Counter ions of the double layer are in dynamic equilibrium with those of the exchanger phase. Introducing foreign counter ions into the external solvent results in these mixing with and displacing the original counter ions of the diffuse layer, allowing them to enter and occupy sites within the exchanger.

Electrolyte exclusion and electroselectivity

The presence of the Donnan potential at the exchanger-solution interface also gives natural explanation to the fact that ion exchangers are permselective to their counter ions. In other words, an ion exchanger will virtually exclude all co-ions, allowing only counter ions into the exchanger phase.

Referring once again to Figure 2.1, it can be seen that should the co-ion (in this case the solution anion) approach the pore it would experience an electrical repulsion from the negatively charged matrix and so have little tendency to enter the pore volume. The Donnan potential automatically favours counter ion exchange and co-ion exclusion. Without further complication for our model we may consider the effect of valency upon ion selection and exclusion of an exchanger.

Since an electrical potential is defined as a force per unit charge, it follows that the larger the charge upon a co-ion, the more efficiently will it be excluded, while in the same manner counter ions of high valency will be preferred; the electroselectivity term.

Selectivity of an ion exchange for counter ions

A typical ion exchange reaction is one in which a sample of the exchanger particle or beads in the A form is added to a stirred solution containing counter ion B. Since the rate of a chemical reaction is determined by its slowest kinetic step, it is advisable to consider these steps in turn. Even in a well-stirred solution there remains a layer of unstirred solution close to any solid surface which may be immersed in that solution. In particular around an exchanger bead, there will be such a layer which under good stirred conditions will be of the order of 10^{-3} cm thick. Being unstirred, the only manner in which the ion may cross will be by diffusion; the film diffusion step. Therefore, there are three distinct kinetic processes:

- (1) Film diffusion in the unstirred layer of solution close to the exchanger particles.
- (2) Particle diffusion of ions in the matrix.
- (3) Chemical exchange reaction.

Of all the exchange kinetics which have appeared in the literature to date, none have been shown to be controlled by the chemical exchange step. In practice, the exchange kinetics to be controlled by

diffusion steps in the film or in the exchange matrix: film diffusion and particle diffusion, respectively.

On the basis of the film theory,⁽⁵⁾ the ion-exchange reaction is seen to be controlled by two simultaneous diffusion steps i.e., diffusion through the Nernst film, and diffusion through the ion exchanger grain. Since the non-steady conditions of diffusion are involved, the Fick's second law is employed.

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (2.1)$$

Each diffusing species must follow this law, in both the film and the ion-exchanger grain. If the diffusion of A in one direction is conditional upon the diffusion of B in the opposite, the diffusion coefficients of which are denoted by D_A and D_B respectively. The concentration gradients are equal and so are the fluxes of A and B in the ion-exchanger. Hence for a given pair of ions, there is only a single exchange diffusion coefficient \bar{D} , for the ion-exchanger phase.

At the solution-ion exchanger interface, an equilibrium can be rapidly set up and maintained, A^+ and B^+ are distributed to different degrees in each phase. This situation can be represented by a chemical equation:



The barred species are in the exchanger phase and R^- represents one fixed charge on the exchanger matrix. Two points are to be noted. The first is that the reaction is reversible and will achieve equilibrium. The second is that the co-ion is not involved in the process hence equation (2.2) may be written more simply:



If diffusion coefficients, D_A , D_B , \bar{D} are treated as constants throughout, the usual law of mass action can be applied in the computation of K , the equilibrium constant, for the reaction

$$K_A^B = \left(\frac{\bar{a}_B^+}{\bar{a}_A^+} \right) \left(\frac{a_A^+}{a_B^+} \right)$$

K_A^B is actually termed selectivity coefficient since it measures the tendency of the exchanger to select B over A.

In experimental practice there is a considerable use of the concentration term in selectivity coefficient. Thus,

$$K_A^B = \frac{[\bar{B}^+][A^+]}{[\bar{A}^+][B^+]} \quad (2.4)$$

Where [] represents the concentration of the respective ions in mole/litre.

If K_A^B is greater than unity, the exchanger selects ion B. If it is less than unity, it selects ion A and if it is equal to unity then the exchanger shows no preference for either ion. Concentrations may be measured in molal, or equivalent fraction units.