Studies on Membrane Equilibria in Multicomponent Systems

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In the present work membrane equilibria in multicomponent systems, where one of the components is a polymer, impermeable through the membrane, have been studied. A theoretical treatment of the problem is presented, and special considerations are given effects arising from the binding of the permeable components by the polymer. It is shown that the equilibrium distribution of the permeable components can be described by a gross equilibrium constant, which contains the binding constant for the permeable solute and an excluded volume term. The latter is related to the solvation of the polymer by the solvent. The treatment is also applied to polyelectrolyte solutions, and it is shown that in these solutions, in addition to the Donnan effect, the excluded volume effect is also present. Experimental results from measurements on polyoxyethylene, polymethacrylic acid and dextran in aqueous solutions are reported. The results were found to be in agreement with the theoretical considerations.

The present investigation deals with membrane equilibria in multicomponent systems, where one of the components is a polymer, impermeable through the membrane and the other components all are permeable. The equilibrium conditions in such systems are specified by the osmotic pressure and the equilibrium distribution of the permeable components.

Such systems are of interest for osmotic measurements with mixed solvents. Also, from the knowledge of the equilibrium distribution of the permeable components, information on the interactions between the polymer-permeable components may be obtained.

We will here first give a theoretical treatment of the problem, based on equilibrium thermodynamics, and present then experimental data from measurements carried out on some polymers in aqueous systems.

THEORETICAL

We will first consider the thermodynamic equilibrium conditions for membrane equilibria in multicomponent systems. The problem has in more or less general form been treated in numerous recent publications, notably in those by Scatchard,[1] Staverman *et al.*[2], Strauss and Ander[3] and Eisenberg.[4]

Here a somewhat different approach will be used. For convenience we will restrict the treatment to three components, the generalisation to a greater number of components being obvious. The components will be designated in the following way: component 1 — solvent, component 2 — permeable solute, component 3 — polymer.

The equilibrium conditions are obtained by equating the chemical potentials for the permeable components on the two sides of the membrane. The chemical potential of a component may be treated as a function of pressure, the mole fraction of the component and its activity coefficient. Taking the solution on the "solvent side" of the membrane as reference, we may expand the chemical potential into a Taylor series around this state. Using conventional notations and retaining only first order terms, we get

$$\mu_i(p + \pi, f_i + \Delta f_i, x_i + \Delta x_i) = \mu_i(p, f_i, x_i) + \frac{\partial \mu_i}{\partial p} \pi + \frac{\partial \mu_i}{\partial f_i} \Delta f_i + \frac{\partial \mu_i}{\partial x_i} \Delta x_i \quad (1)$$

The first differential coefficient in (1) is equal to the partial molar volume v_i; the other two may be obtained from the expression for chemical potential at constant pressure

$$\mu_i = \mu_i^\circ + RT \ln f_i x_i \quad (2)$$

Hence the equilibrium conditions become

$$v_1 \pi + RT \frac{\Delta f_1}{f_1} + RT \frac{\Delta x_1}{x_1} = 0 \quad (3)$$

$$v_2 \pi + RT \frac{\Delta f_2}{f_2} + RT \frac{\Delta x_2}{x_2} = 0 \quad (4)$$

From these equations expressions for the osmotic pressure and the distribution of permeable components may be obtained.

To obtain an expression for the osmotic pressure we add (3), multiplied by x_1, to (4), multiplied by x_2. Observering that

$$x_1 v_1 + x_2 v_2 = v \quad (5)$$

where v is the molar volume of the mixture of components 1 and 2, we then get

$$\frac{v\pi}{RT} = -(\Delta x_1 + \Delta x_2) - \left(x_1 \frac{\Delta f_1}{f_1} + x_2 \frac{\Delta f_2}{f_2} \right) \quad (6)$$

As

$$x_1 + x_2 + x_3 = 1 \quad (7)$$

we get for the first term in the right member of (6)

$$-(\Delta x_1 + \Delta x_2) = \Delta x_3 \quad (8)$$

To evaluate the second term we use Gibbs-Duhems equation for the activity coefficient

$$\sum_i x_i \, d \ln f_i = 0 \quad (9)$$

We now let x_3 on the solvent side be zero and choose the standard state in such a manner that

$$f_3 = 1 \text{ when } x_3 = 0$$

With x_3 as the independent variable eqn. (9) may be integrated in the form

$$\int_0^{\Delta x_3} x_1 \frac{\mathrm{d} \ln f_1}{\mathrm{d} x_3} \mathrm{d} x_3 + \int_0^{\Delta x_3} x_2 \frac{\mathrm{d} \ln f_2}{\mathrm{d} x_3} \mathrm{d} x_3 = - \int_0^{\Delta x_3} x_3 \frac{\mathrm{d} \ln f_3}{\mathrm{d} x_3} \mathrm{d} x_3 \qquad (10)$$

Using power series expansions for x_1 and x_2 and the mean value theoreme, the integrals in the left member take the form

$$\int_0^{\Delta x_3} (x_i + a_i x_3 + \cdots) \frac{\mathrm{d} \ln f_i}{\mathrm{d} x_3} \mathrm{d} x_3 = x_i \Delta \ln f_i + a_i \Theta \Delta x_3 \Delta \ln f_i + \cdots \qquad (11)$$

where $0 > \Theta > 1$.

For the right member of (10) we get by partial integration

$$-\Big]_0^{\Delta x_3} x_3 \ln f_3 + \int_0^{\Delta x_3} \ln f_3 \, \mathrm{d} x_3 \qquad (12)$$

Assuming that $\ln f_3$ may be expanded into the power series

$$\ln f_3 = a \, x_3 + \beta \, x_3^2 + \cdots \qquad (13)$$

we get for (12)

$$-\tfrac{1}{2} \Delta x_3 \ln f_3 - \tfrac{1}{6} \beta \, (\Delta x_3)^3 - \cdots \qquad (14)$$

Using (11) and (14), and neglecting higher order terms, we get for (10)

$$x_1 \frac{\Delta f_1}{f_1} + x_2 \frac{\Delta f_2}{f_2} = - \tfrac{1}{2} \Delta x_3 \ln f_3 \qquad (15)$$

With (8) and (15) eqn. (6) reduces to

$$\frac{v \pi}{RT} = \Delta x_3 \left(1 + \tfrac{1}{2} \ln f_3\right) \qquad (16)$$

This equation, which is valid in dilute solutions, is of some importance. It is of the same form as the equation for osmotic pressure in a two-component system, the only difference being that the partial molar volume for the solvent has been replaced by the molar volume of the composite solvent. It shows that in osmotic molecular weight determinations the use of multicomponent solvents is perfectly admissible.

We will now examine the equilibrium distribution of the permeable components. It is convenient to introduce the following relation

$$v_2 = n \, v_1 \qquad (17)$$

After eliminating π from (3) and (4) we then get

$$\Delta x_1 = \frac{x_1 \Delta x_2}{n \, x_2} + \frac{x_1}{n} \left(\frac{\Delta f_2}{f_2} - n \frac{\Delta f_1}{f_1}\right) \qquad (18)$$

Using (8) and (18) we finally get

$$\Delta x_1 = - \frac{x_1 \Delta x_3}{x_1 + n x_2} + \frac{x_1 x_2}{x_1 + n x_2} \left(\frac{\Delta f_2}{f_2} - n \frac{\Delta f_1}{f_1}\right) \qquad (19)$$

and

$$\Delta x_2 = - \frac{nx_2\,\Delta x_3}{x_1 + nx_2} - \frac{x_1 x_2}{x_1 + nx_2}\left(\frac{\Delta f_2}{f_2} - n\,\frac{\Delta f_1}{f_1}\right) \tag{20}$$

These equations show that the changes in the mole fractions of the permeable components split into two terms. One "ideal term" depends on the change in the mole fraction of the polymer and on the relative magnitudes of the partial molar volumes of the permeable components. The other "nonideal term" is due to the interaction with the polymer and is expressed in terms of the activity coefficient increments of the permeable components.

We will now consider the ideal case. Then, by definition

$$\Delta f_1 = \Delta f_2 = 0 \tag{21}$$

and (19), (20) become

$$\Delta x_1 = - \frac{x_1\,\Delta x_3}{x_1 + nx_2} \tag{22}$$

$$\Delta x_2 = - \frac{nx_2\,\Delta x_3}{x_1 + nx_2} \tag{23}$$

For the "solution side" we now get

$$\frac{x_1 + \Delta x_1}{x_2 + \Delta x_2} = \frac{x_1(x_1 + nx_2) - x_1\,\Delta x_3}{x_2(x_1 + nx_2) - nx_2\,\Delta x_3} = \frac{x_1}{x_2}\frac{x_1 + nx_2 - \Delta x_3}{x_1 + nx_2 - n\,\Delta x_3} \tag{24}$$

This shows that even in the ideal case, provided $n \neq 1$, the distribution of the permeable components is unequal on the two sides of the membrane.

If $n > 1$

$$\frac{x_1 + \Delta x_1}{x_2 + \Delta x_2} > \frac{x_1}{x_2} \tag{25}$$

which shows that the permeable component with the smaller partial molar volume is enriched on that side of the membrane where the pressure is higher. However, from (24) it is quite obvious that the effect is negligibly small in macromolecular systems, as then $\Delta x_3 << 1$.

From measurements of the osmotic pressure and the distribution of the permeable components it would be possible to determine the activity coefficient increments for all components. From (16) the activity coefficient for the polymer is obtained and from (15), together with (19) or (20), the activity coefficient increments for the permeable components follow.

The activity coefficients so determined are of a somewhat formal nature. They refer to the total concentrations of the permeable components and thus do not take into account association effects between the polymer and the permeable components. In the following we will take this effect also into account and we will now derive an equation that connects the variables in eqn. (20) to measurable quantities. As from the viewpoint of experimental accuracy the solutions are best prepared by weighing the different components, we will use weight concentrations.

The concentrations of the permeable solute (component 2) and polymer (component 3) will be given in the following way:

c_2: m moles per 1 kg of solution,

c_3: c g per 1 kg of solution.

We will further designate the molecular weights of the components 1, 2 and 3 by M_1, M_2 and M_3, respectively.

On the solvent side, by definition

$$x_2 = m \bigg/ \left(m + \frac{1000 - m\,M_2)}{M_1} \right) \qquad (26)$$

For the analogous expression on the solution side we take into account the binding of components 1 and 2 by the polymer. Hence

$$x_2 + \varDelta x_2 = \cfrac{m + \varDelta m - \varDelta m_1}{m + \varDelta m - \varDelta m_1 + \dfrac{c}{M_3} + \dfrac{1000 - (m + \varDelta m)M_2 - c - \gamma}{M_1}} \qquad (27)$$

where

$\varDelta m$ = total change in c_2 (in moles per 1 kg of solution)

$\varDelta m_1$ = the amount of component 2 bound by the polymer (in moles per 1 kg of solution)

γ = the amount of component 1 bound by the polymer (in g per 1 kg of solution)

Dividing (27) by (26) we get

$$1 + \frac{\varDelta x_2}{x_2} = \cfrac{1 + (\varDelta m - \varDelta m_1)/m}{1 + \dfrac{M_1[\varDelta m - \varDelta m_1 + (c/M_3)] - \varDelta m\, M_2 - c - \gamma}{1000 + m\,(M_1 - M_2)}} \qquad (28)$$

For dilute solutions (low values of m and c) we get, after some obvious approximations

$$\frac{\varDelta x_2}{x_2} = \frac{\varDelta m - \varDelta m_1}{m} + \frac{c + \gamma}{1000} \qquad (29)$$

Using (20) and (29) and observing that the ideal term in the former equation is negligible, we get:

$$\frac{\varDelta m}{m} + \frac{c}{1000} = \frac{\varDelta m_1}{m} - \frac{\gamma}{1000} - \frac{x_1}{x_1 + nx_2}\left(\frac{\varDelta f_2}{f_2} - n\, \frac{\varDelta f_1}{f_1} \right) = \delta \quad (30)$$

In this equation the left member represents an experimentally determinable quantity and we will designate it by δ. For low degrees of binding of component 2, we may assume the different binding sites to be independent of each other. The mass action law then gives

$$k = \frac{\varDelta m_1}{[(c/M) - \varDelta m_1)]m}$$

or

$$\varDelta m_1 = \frac{k\,c\,m}{M(1 + km)} \qquad (31)$$

where k is the equilibrium constant for the binding reaction and M is the equivalent weight of the polymer. In the same way, we get for γ in dilute solutions (component 1 in large excess).

$$\gamma = ac \qquad (32)$$

Substituting (31) and (32) into (30) we get

$$\delta = \left(\frac{k}{M(1 + km)} - \frac{\alpha}{1000} \right) c - \frac{x_1}{x_1 + nx_2} \left(\frac{\Delta f_2}{f_2} - n \frac{\Delta f_1}{f_1} \right) \qquad (33)$$

In this equation the right member contains four unknowns, namely the two activity coefficients and the binding constants α and k. Obviously they are not all determinable. It would be possible to put both α and k conventionally equal to zero and let all deviation from ideality be determined by the activity coefficients alone. A similar procedure is often used in the case of low molecular weight substances. As mentioned above it would then be possible to determine all the activity coefficient increments if the osmotic pressure was simultaneously measured. However, this procedure seems not advisable in polymeric systems. as it would lead to an incorrect concentration dependence of the activity coefficients. To see this we recall that the analytical form of the activity coefficient in a binary mixture (see any standard textbook in thermodynamics) is:

$$\ln f_1 = \sum_k a_k \, x_2^{\lambda_k} \qquad (34)$$

where for nonelectrolyte solutions in general $\lambda_1 = 2$ and for electrolyte solutions, where long range forces are operative, $\lambda_1 = 1.5$.

It is reasonable to assume the same concentration dependence in multicomponent systems. It would then be possible to express the limiting concentration dependence of the activity coefficient term in (33) in the form

$$\frac{x_1}{x_1 + nx_2} \left(\frac{\Delta f_2}{f_2} - n \frac{\Delta f_1}{f_1} \right) = \beta \, c^\lambda \qquad (35)$$

with $\lambda \geqslant 1.5$.

After division by c (33) would then take the form

$$\frac{\delta}{c} = \left(\frac{k}{M(1 + km)} - \frac{\alpha}{1000} \right) - \beta \, c^{\lambda - 1} \qquad (36)$$

Thus, if k and α were put equal to zero δ/c would tend to zero with c. This, however, is contrary to experimental observations, Fig. 3, and we conclude that the first term in (36) is physically significant. We will now turn our attention to the experimental side of the problem and will later give an interpretation of eqn. (36) in the light of the experimental results.

EXPERIMENTAL

The studies of the membrane equilibria were carried out in a cell of the form shown in Fig. 1. It was essentially an enlarged block-type osmometer cell made of polyethylene. The volume of each half-cell was 40 ml. The membrane was a commercial cellophane membrane ("sausage-casing" from The Visking Corp., Chicago). The equilibra-
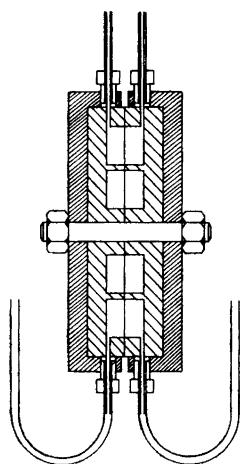
Fig. 1. The dialysis cell. The polyethylene cell is supported by a brass cover and held together by a central screw. The cell is filled and emptied through polyethylene tubes.

tion of the solutions was carried out in an air box inside a water thermostat, at 25°C for about 24 h. This was well in excess of the actual time necessary for attainment of equilibrium, which was found by trial to be of the order of 4 h. The experiments were carried out with three different polymers. They had the following characterizations:

Polyoxyethylene (POE). The sample was purified by precipitating the polymer from a solution in a benzene-ethanol mixture with hexane. $DP_w \approx 10\ 000$.

Polymethacrylic acid (PMA). The sample was purified by precipitating the polymer from a solution in methanol with ethyl ether. $DP_w \approx 1300$.

Dextran. The sample was purified by precipitating the polymer from a solution in water with ethanol. $DP_w \approx 940$.

The choice of the permeable solute was limited by the analytical method used for the concentration determination. In principle all accurate chemical or physical methods for concentration determination can be used in this connection. In the present experiments use was made of the acid-base titration method. Owing to the simplicity and high accuracy of this method it was well suited for this type of measurements. In the present work alkali, mostly sodium hydroxide, was used as the permeable solute.

We will now present the experimental results obtained with the different polymers.

POE. In these experiments only NaOH was used as the permeable solute. The general experimental procedure was the following. The equilibrated solutions were removed from the cell and aliquots of 25 ml of each solution were transferred with a pipette to glass stoppered flasks and weighed. Most of the alkali in the solutions was then neutralized by adding to each solution 25 ml of a standard HCl solution with a precision pipette. The final neutralization of the alkali was then carried out by titrating with a 0.05 M HCl solution using a microburette and with phenolphthalein as indicator. By this method the concentrations of NaOH in the two solutions could be determined with a relative accuracy of about 0.01 %. Two different series of measurements were undertaken. In one the concentration of POE was kept constant and the concentration of NaOH varied, while in the other these conditions were reversed. The results are shown in the form of diagrams, Figs. 2 and 3.

PMA. Here NaOH was used as the permeable solute and the general experimental procedure was the same as with POE. The titration of the solution containing PMA was carried out to the point where only the excess NaOH was neutralized and the PMA was left in the form of its Na-salt. A titration curve of PMA in the presence of an excess of NaOH is shown in Fig. 4 and we see that there is a distinct equivalence point in the
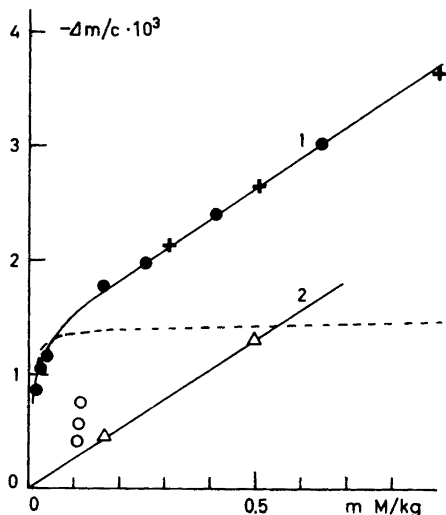
Fig. 2. Measurements with POE and PMA at constant polymer concentration. Curve 1 for PMA with $c = 5.2$ g/kg; curve 2 for POE with $c = 4.5$ g/kg. Open circles represent Δm for NaOH in PMA solutions in the presence of NaCl, from top to bottom $m_{NaCl} = 0.20$, 0.40 and 0.80 M/kg. The crosses on curve 1 represent the corresponding Δm values referring to the total permeable electrolyte concentration. Dotted curve represents eqn. (40) with $c = 5$ g/kg and with $\varepsilon = 0.25$.
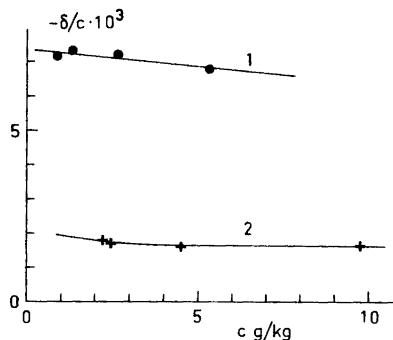
Fig. 3. Measurements with POE and PMA at constant NaOH concentration. Curve 1 for PMA with $m = 0.25$ M/kg; curve 2 for POE with $m = 0.5$ M/kg.

vicinity of pH 10. The titration of the solutions was here carried out with thymolphthalein as indicator (pH interval 9.3—10.5) and the color change interval was found to be quite narrow. Measurements were carried out both at a constant PMA concentration, varying the NaOH concentration, and *vice versa*. Some measurements were also carried out with NaOH in the presence of varying amounts of NaCl. The Δm-values for NaOH were depressed by the presence of NaCl. However, assuming that NaCl is displaced to the same extent as NaOH, and calculating Δm for the total amount of permeable electrolyte, the same results were obtained as in pure NaOH solutions. The results are shown in Figs. 2 and 3.
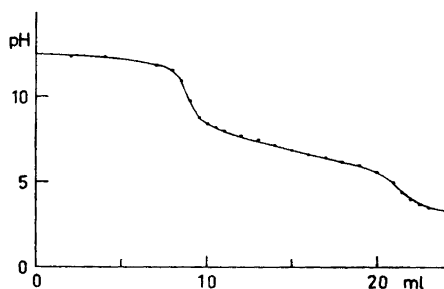

Fig. 4. Titration curve for PMA in the presence of an excess of NaOH.

Dextran. In these experiments the general procedure was the same as in the case of the other polymers. However, here a certain binding of alkali occurred, owing to the acidic nature of the hydroxyl groups in dextran. The binding was so weak, however, that the titration curve for the alkali was not affected by the presence of dextran. Therefore at the equivalence point all alkali was neutralized. The indicator used was phenolphthalein. In these experiments the permeable solutes were NaOH and NaOH in the presence of neutral salt (NaCl).
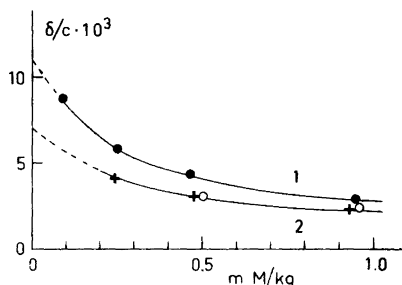

Fig. 5. Measurements with dextran in NaOH solutions. Curve 1 for solutions with 0.5 M NaCl and with $c = 6.8$ g/kg, curve 2 for solutions in pure NaOH and with $c = 8.5$ g/kg. Open circles on curve 2 refer to a dextran concentration of $c = 3.1$ g/kg.

The results are shown in Fig. 5. We see that the dependence of δ/c on the alkali concentration is of the form predicted by eqn. (36) and that practically no dependence on the polymer concentration can be observed. It is interesting to note that the presence of NaCl increases the acid strength of dextran. This is in accord with observations made by other workers.[5]

DISCUSSION

In deriving eqn. (33), the basic equation determining the distribution of the permeable solute, we introduced four parameters. It now remains to examine their physical significance. As already mentioned, the experimental results showed that the chemical binding term, $[k/M(1 + km)] - 0.001\ \alpha$, in (36) is in general different from zero and therefore a description of the equilibrium situation with the help of the activity coefficients alone is not possible. The sign of this binding term depends on the relative magnitudes of the binding constants k and α for the permeable solute and the solvent respectively. Both positive and negative signes were found in the present experiments.

The parameter α was introduced to take into consideration the binding of solvent by the polymer. This "chemically bound" solvent was considered to be inaccessible for the permeable solute. One might feel tempted to consider this solvent to constitute the "solvating solvent" of the polymer. However, as it appears from later discussion, this interpretation of the effect would be more or less arbitrary. Thus, as the exact mechanism of interaction is unknown the effect could more adequately be termed the "excluded volume" effect. Then, formally, α is the amount of solvent per 1 g of polymer from which the permeable solute is excluded.

The parameter k is the equilibrium constant for the binding of the permeable solute by the polymer. It is important to note that a separate determination of k and α is not possible. Only the composite term, $(k/M) - 0.001\ \alpha$, is experimentally determinable and it is obtained by extrapolating (36) to zero concentrations of the polymer and the permeable solute. It can be looked upon

as the gross equilibrium constant for binding of the permeable solute. We may designate it by K, thus

$$K = \frac{k}{M} - \frac{\alpha}{1000} \tag{37}$$

In the case any binding of the permeable solute by the polymer can be precluded from chemical reasons, k can a priori be put equal to zero. In this case the determination of K would yield the excluded volume paramter α. This is probably the case with POE. From Fig. 3 we thus get $\alpha = 1.7$ g of water per g of POE.

The experiments with dextran in NaOH solutions show that it is possible by membrane equilibrium studies to determine the gross binding constant rather accurately even for very slight binding effects. The gross equilibrium constants for dextran, obtained from measurements in solutions of pure NaOH, and NaOH in the presence of 0.5 M NaCl, are $K = 7 \times 10^{-3}$ and $K = 11 \times 10^{-3}$, respectively. From the equilibrium constant in NaOH solutions we may calculate the thermodynamic acid dissociation constant K_s for a glucose unit. As the experimental K-value was obtained by extrapolating to zero electrolyte concentration, the concentrations in eqn. (31) may be replaced by the corresponding activities and we get

$$k = \frac{a_{RO^-}}{c_{ROH}\, a_{OH^-}} = \frac{a_{RO^-} \cdot a_{H^+}}{c_{ROH}\, K_w} = \frac{K_s}{K_w} \tag{38}$$

where K_w is the ionic product of water. Using the values $M = 162$ and $K_w = 10^{-14}$ and neglecting the excluded volume term in (37) we get $K_s = 1.1 \times 10^{-14}$ at 25°C. For free glucose we get from the literature[6] $K_s = 3.7 \times 10^{-13}$ at 18°C. Thus, there is a substantial difference in the acidity constants for a glucose unit in dextran and for free glucose.

The present treatment can also be applied to Donnan equilibria, encountered with polyelectrolytes. We will first compare the experimental results with the classical Donnan theory. With the present notations the following relation is obtained.

$$m^2 = (m + \Delta m)\,[m + \Delta m + (c\varepsilon/M)] \tag{39}$$

where M is the equivalent weight of the polyelectrolyte and ε its degree of dissociation. Solving (39) for Δm we get

$$\Delta m = - [m + (c\varepsilon/2\,M)] + \sqrt{m^2 + (c\varepsilon/2M)^2} \tag{40}$$

In Fig. 2, together with the experimental data, a curve representing eqn. (40) for PMA with $c = 5$ g/kg and with $\varepsilon = 0.25$ is shown. We see that at very low salt concentrations the agreement with (40) is excellent. At higher salt concentrations, according to the Donnan theory, Δm should asymptotically approach a constant value with increasing m, whereas the experiments indicate that Δm increases linearly with m. This concentration dependence, on the other hand, is predicted by the excluded volume effect (36). It thus appears that in polyelectrolyte solutions these two effects are superposed. We will now give an explanation of the behaviour of polyelectrolyte solutions in terms

of the excluded volume effect. We will base the present treatment principally on macroscopic considerations.

The equilibrium situation in a macroscopic system is adequately described in terms of activities. If actual chemical binding occurs and this is taken separately into account, the concentrations of the different species are specified and the activities are unequivocally determined by the activity coefficients. Thus, the whole situation can be described by the activity coefficients and the equilibrium constants for chemical binding.

The situation in a polymer solution is complicated by the fact that these solutions are inherently inhomogeneous. The concentration of polymer segments is highest in the center of gravity of a polymer molecule and decreases gradually in the outward direction. In dilute solutions the domains of different polymer molecules are separated and the concentration of polymer segments is zero in the intermolecular space between the polymer molecules. In concentrated solutions the domains overlap to a certain extent and variations in the segment density are less pronounced. It is obvious that in such systems the true activity coefficients and the equilibrium constants for chemical binding (both defined over microscopic regions) vary from point to point and the quantities entering eqn. (33) are thus special average values over the domain under consideration. For the activity coefficients these averages are the ones that the membrane "feels" and they may be termed the "membrane average" values of the activity coefficient. Of course, an evaluation of these averages requires specified models for the macromolecule and its interactions with the solvent and the permeable solute, as well as for the functioning of a semipermeable membrane, and at present none is sufficiently developed. However, it is easy to see, that the gross macroscopic effect of such an averaging process gives rise to the excluded volume term in the equilibrium equations. Assuming that in dilute solutions the "membrane average" activity coefficients are primarily determined by the activity coefficients in the intermolecular space between the polymer molecules it follows that their increments would tend to zero with the polymer concentration. On the other hand the activity coefficients inside the domain of a polymer molecule, which determine the permeable solute concentration in that domain, would essentially be independent of the polymer concentration and would thus give rise to the constant "excluded volume" term in eqn. (36).

In polyelectrolyte solutions this term appears to be very large at low salt concentrations. We may assume that it is due to Donnan equilibria set up between the domains of the polyelectrolyte molecules and their surroundings and thus is determined by eqn. (40). At higher salt concentrations the amount of salt excluded by this mechanism becomes essentially constant and the additional exclusion of salt found in the experiments must be due to some other mechanism in which the exclusion is proportional to the salt concentration and thus gives rise to a constant excluded volume factor. The latter occurs even with non-electrolyte polymers and probably the effect is of the same nature in both cases.

It should be mentioned here that an explanation of the Donnan effect in terms of an "excluded volume" effect has been offered by Strauss and Ander[3] in a study of membrane equilibria with polyphosphate solutions. They sug-

gested that the excluded volume effect is due to the exclusion of the permeable salt from the counterion atmosphere, surrounding the polyelectrolyte chain.

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