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Modelling Reverse Osmosis

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After a brief presentation of the principal kinetic and thermodynamic aspects of the theory of reverse osmosis, the present review examines various physicochemical mechanisms of the selectivity of membranes with respect to electrolyte solutions: the electrochemical mechanism, related to the charge of the pore surface; the dielectric exclusion of ions, due to image forces; and the structural mechanism, due to the change in the properties of water in fine hydrophilic pores. Methods for calculating the changes in the standard chemical potentials of ions on entering the membrane phase, and the effects of the Donnan exclusion of ions with allowance for the different charge of the membrane have been described. It has been concluded that it is appropriate to use charged membranes to separate electrolyte solutions at low concentrations. The problem of the transport of solutions through the fine pores of membranes has been formulated, taking account of the equilibrium distribution coefficients of the ions, their mobility, the charge of the membrane, and the phenomenon of concentration polarisation. Routes to the further development of the theory as applied to membranes of different types, different compositions, and solution concentrations have been discussed.
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I. INTRODUCTION

The desalination of aqueous solutions by reverse osmosis is finding increasing practical application because of the much smaller quantity of energy required for membrane separation. This raises the question of the development of a theory of reverse-osmosis separation, which can be constructed using different mathematical and physical models of membranes and different physicochemical theories of the mechanism of their selectivity. The present review examines the effect on the selectivity of membranes of the charge on the pore surface, the dielectric and Donnan exclusion of ions from the membrane phase, and the structural changes in water in fine pores.

A distinguishing feature of the approach developed here is that it takes account of the influence of the fields of long-range surface forces on the equilibrium and on the transport of the solutions in membranes. As shown below, the main predictions which follow from the theoretical examination of the reverse osmosis of electrolyte solutions are confirmed experimentally.

II. KINETIC AND THERMODYNAMIC ASPECTS OF THE THEORY OF REVERSE OSMOSIS

In the reverse-osmosis desalination of solutions, the liquid which has passed through the membrane contains less dissolved substance than the liquid entering the membrane. The ability of a membrane to separate a substance is characterised quantitatively by its selectivity

$$\varphi = 1 - (c_2/c_0) \qquad (1)$$

where c_0 and c_2 are the concentrations of the salt in the original solution and beyond the membrane respectively. In the present review, for simplicity, only a binary uni–univalent electrolyte will be examined.

The excess of the salt in front of the membrane is removed continuously by the tangential flow of liquid, which ensures a steady-state process. Since the solvent passes through the membrane, whereas the salt is retained to some extent, its concentration directly at the front surface of the membrane, that is on the high-pressure side, is higher than its concentration in the incoming stream. The diffusion boundary layer produced in this way in front of the membrane is usually called the concentration polarisation layer.

The quantity of salt retained by the membrane in unit time is given by the difference $vc_0 - vc_2$, where v is the linear velocity of the liquid. This excess of salt is removed from the membrane surface by the diffusion flux, which is directed in the opposite direction to the convective flow and which can be expressed in terms of the thickness of the diffusion layer:

$$vc_0 - vc_2 = -D_e \operatorname{grad} c|_{x=0} \sim D_e \frac{c_0 - c_1}{\delta} \qquad (2)$$

where $D_e = (D^+ + D^-)/2$ is the effective diffusion coefficient of the ions in the free solution, and c_1 is the concentration of the salt at the front surface of the membrane. The description of the external-diffusion kinetics in reverse osmosis has been the subject of a large number of studies (see Ref.1); it reduces to the solution of the equation for convective diffusion with the boundary condition (2), which can be expressed in terms of the membrane selectivity, usually

assumed to be given. The concentration polarisation is also usually assumed to be known in the examination of internal-diffusion kinetics.

In the description of the steady-state process of reverse osmosis, it will be assumed that the applied pressure difference and the flux of the liquid Q are given, that there is no transfer of charge through the membrane ($I = 0$), and that the quantities Q,I, and the salt flux J_s are the same in all sections of the membrane. Since the transport of the salt is purely convective in the free solution beyond the membrane,[2-4] this leads to the important boundary condition:

$$c_2 = c|_{x=h} = J_s/2Q \qquad (3)$$

where h is the thickness of the dividing layer of the membrane. This condition makes it possible to express the unknown quantity c_2, which cannot be calculated directly, in terms of the other quantity J_s, which is also unknown but which can be calculated. For this purpose, the membrane model must be specified.

Reverse osmosis results from the difference between the kinetic and equilibrium properties of the solution in the pores of membrane and in the bulk. Different workers have related the decrease in the salt flux through the membrane to the decrease within the membrane in either the velocity or the concentration of the ions. This distinction, which is sometimes encountered in the literature, is unjustified, since the principal role may be played by either factor, depending on the properties of the membrane.

Ion transport in biological membranes[5] and concentrated dispersions (pastes)[6] has been more extensively studied than reverse osmosis. Reverse-osmosis membranes occupy an intermediate position between biological membranes and the systems which are the traditional objects of study in colloid science. Reverse-osmosis membranes with very fine pores are closer to biological membranes, and those with relatively large pores are closer to traditional colloid-chemical systems.

One of the difficulties of modelling reverse-osmosis processes is due to the wide variety of processes influencing demineralisation. Frequently, however, it is possible to distinguish the process predominating for given pore dimensions.

When reverse-osmosis membranes with very fine pores are used, a factor which also appears in biological membranes becomes important, namely the commensurability of the dimensions of the hydrated ion and the pore (the ion channel in biological membranes). A hydrated ion cannot penetrate into a pore with sufficiently small dimensions,[7] and this predetermines the ideal semi-permeability of the membrane. The difference between the observed selectivity and the maximum possible selectivity is probably due to the presence in the membrane of pores with different dimensions. If the dimensions of the hydrated ion are smaller than but close to those of the pore, the rate of flow of the liquid in the pore containing the ion is lowered. Since for a moderate salt concentration a large fraction of the pores do not contain ions, the average rate of ordered movement of the ions of the salt may be appreciably lower than the average rate of flow of the liquid.

In real membranes, the pores have a variable cross-section. As a result, both the pore dimensions and the molecular forces of the interaction of the ion with the pore walls change along its path. These changes can be described by regarding them as a series of energy barriers and potential wells. Here, the Eyring method for describing ion transport, widely used in the examination of biological membranes,[5] may prove useful. For membranes whose pore dimensions are commensurate with those of the hydrated ions, kinetic factors also become important; in this case there may be considerable deviations from equilibrium.[8,9]

Decrease in the pore dimensions leads to an increase in the selectivity of the membranes, but at the same time their efficiency decreases. It is therefore appropriate to decrease the thickness of the dividing layer of the membrane while at the same time increasing its porosity. This trend in the technology of reverse osmosis in the last ten years has led to considerable progress, associated with the production of so-called composite membranes, which show simultaneously high selectivity and efficiency.[10-12] Composite membranes also have certain disadvantages, however. The technology of their production is still complex and expensive, and the actual membranes are inconvenient in use, in particular because of their high sensitivity to mechanical damage. Progress in the use of composite membranes probably depends primarily on progress in the technology of their production.

One widely used model is the homogeneous model of a membrane.[13,14] Its characteristic feature is the possibility of any ion path, whereas in the heterogeneous model it is assumed that ion transport takes place only through the pores. In the homogeneous model it is assumed that the ions can be regarded as dissolved in the membrane. Research workers have encountered considerable difficulties in validating this model.[15] The reason is that real membranes are not perfect or free from defects, and in transport processes the defects behave like pores. In this connection, some authors[16,17] have considered two possible ion transport paths in a membrane: through the pores and through homogeneous regions.

It is appropriate to divide membranes into porous and diffusion membranes.[18] The latter are quasi-homogeneous gels, through which the solvent and the dissolved substance penetrate under the influence of a concentration gradient. These membranes have a high hydrodynamic resistance, so that they must be used in the form of ultra-thin films with a thickness of $0.02-0.04$ μm, fixed to porous supports.

The representation of a membrane as a heterogeneous system is much more widely encountered. Dytnerskii's capillary-filtration model of selective permeability[7] is applicable only in this representation. The familiar model of Sourirajan[19] combines the representations of flow through pores and of preferential adsorption of the dissolved substance or the solvent on the "walls" of the pore.

The increased interest in the heterogeneous model and the importance of taking account of surface forces in this model have been noted.[20-24] Sourirajan's model has also undergone changes in this direction. Previously, in this model, the lowered concentration of the ions in the pores of the membrane was explained using the Gibbs adsorption equation.[19] The limited nature of this approach is indicated by the fact that it does not take account of the pore radius, which is an extremely important parameter in reverse osmosis. In the new improved model,[24] the concentration of ions in the pore is described with allowance for surface forces, which decrease with increasing distance from the pore wall, so that the increase in its radius becomes a factor which lowers the selectivity of the membrane.

The interest in the heterogeneous model of the membrane is not accidental, since it makes it possible to explain a number of features. Firstly, the wider the pore, the more justified becomes the use of the theory of surface forces.[25] On the other hand, the narrower the pore, the lower the accuracy of this theory, and the more difficult the quantitative description of the lowered velocity of the ions. Secondly, the sharp decrease in selectivity with increase in the pore

dimensions makes the wider pores responsible for the "ion leakage" in reverse osmosis. This means that even when the average pore dimensions are commensurate with the dimensions of the hydrated ion, the selectivity due to the presence of a certain proportion of wider pores is still important.

This justifies the particular attention paid in the present work to selectivity mechanisms which operate at pore dimensions appreciably greater than the dimensions of the hydrated ion.

Different levels of the theoretical description of reverse osmosis exist, corresponding to different degrees of detail in the model. At the most descriptive level, the given quantities are the kinetic coefficients characterising the membrane as a whole. In this case, the parameters of reverse-osmosis desalination are found as functions of these coefficients.[25-28] The kinetic coefficients characterising the membrane as a whole are in turn determined by the geometric structure of the membrane, the local values of the concentrations, and the local kinetic characteristics of the solution (such as the viscosity and diffusion coefficients of the components). The specification of these last quantities as parameters of the model and the formulation of the problem of reverse osmosis on this basis move the theoretical description to the next level. The problem of calculating the equilibrium local concentrations in the capillaries of the membrane at the molecular level is now being solved[29] on the basis of the method developed by Yukhnovskii.[30] As far as the more complex problem of calculating the local values of the kinetic coefficients in the membrane at the molecular level is concerned, only the first steps are being taken in this direction, and these coefficients still have to be specified as parameters of the model.

The above two approaches to the theory of reverse osmosis were first combined in Refs.2 and 23. The results obtained are of only limited value, however, since account was taken of only one selectivity mechanism influencing the concentration of ions in the membrane, namely the charge mechanism. Soviet scientists have recently developed a complex approach in the theory of reverse osmosis, with allowance for a variety of mechanisms. This has been the result of systematic studies of surface forces[25] and non-equilibrium electrical surface phenomana[31-33]—a new direction in colloid science.

III. NON-EQUILIBRIUM ELECTRICAL SURFACE PHENOMENA AND REVERSE OSMOSIS

As early as 1947, Deryagin[34] pointed out that the involvement of the electrical double layer in convective ion fluxes should lead (by analogy with the flow potential) to a decrease in the concentration of the dissolved substance between the ends of the capillary. The effect described was detected much later, and was subsequently called reverse osmosis. If this effect is analogous to the flow potential, there should also exist a phenomenon analogous to electro-osmosis, namely slippage in the diffuse atmosphere of the ions or molecules under the influence of the concentration gradient. In Ref.34 the existence of this effect, called capillary osmosis, was justified rigorously on the basis of thermodynamic considerations, but the conclusions applied to the case of a non-electrolyte, that is a diffuse structure of the adsorption layer of the molecules was assumed. The theory of capillary osmosis in electrolytes was developed later using the methods of the thermodynamics of irreversible processes.[35,36]

Osmosis, however, that is the flow of a substance through an ideal selective membrane under the influence of a concentration gradient, can be completely balanced by applying a pressure equal in magnitude to the osmotic pressure. As a result, the flow stops, and the system moves into a state of thermodynamic equilibrium. This constitutes a qualitative difference between osmosis and flow through an ideal membrane, that is capillary osmosis, and this is emphasised by the difference in the names. Thus osmosis is simply a limiting case of capillary osmosis, when the selectivity of the membrane tends to unity. Strictly speaking, non-ideal selective membranes are used for desalination, and it is more correct to call the corresponding process reverse capillary osmosis, and not reverse osmosis.

IV. PRINCIPLES OF THE THEORY OF NEW ELECTROKINETIC PHENOMENA AND REVERSE OSMOSIS

In the examination of reverse osmosis in membranes with relatively wide pores, it is possible to introduce the concept of the convective flow of ions, that is the entrainment of the ions by the flow of liquid. In addition, it is also necessary to take into account the diffusion of the ions relative to the liquid, brought about by the difference between the concentrations of the ions in front of and behind the membrane. This effect, which lowers the selectivity of the membrane, cannot be eliminated completely, but its negative influence can be lowered considerably by increasing the rate of flow to such an extent that the following condition is satisfied:

$$\mathrm{Pe}=vh/D_{\epsilon}\gg 1 \tag{4}$$

The Peclet number Pe can be used to estimate the ratio of the intensities of the convective and diffusion fluxes. When $\mathrm{Pe}\ll 1$, diffusion makes it possible to practically equalise the difference in concentrations at the capillary inlet and outlet. When $\mathrm{Pe}\gg 1$, on the other hand, diffusion is suppressed by the strong convective flux, and the selectivity of the membrane approaches its limiting value. The basic law of conservation of the number of ions under steady-state conditions is given by

$$\operatorname{div} j^{\pm}=0 \tag{5}$$

applied to the one-dimensional problem of flow through a membrane in the form

$$\partial j^{\pm}/\partial x=0 \tag{6}$$

where $j^{\pm}$ represents the densities of the fluxes of the cations and the anions. The main difference between the diffusion-electrical theory of electrokinetic phenomena[31,32] and the classical theory of Smolukhovskii lies in the fact that it shows that it is necessary to use not a single overall law of charge conservation but the laws of conservation for the cations and anions separately. In the diffusion-electrical theory, the expression for the density of the ion fluxes is written taking account of three transport mechanisms: convection, diffusion, and electromigration:

$$j^{\pm}=c^{\pm}(x)\,v-D^{\pm}\frac{\mathrm{d}\,c^{\pm}}{\mathrm{d}\,x}\mp D^{\pm}\frac{F}{RT}c^{\pm}(x)\frac{\partial\psi}{\partial x} \tag{7}$$

where c represents the concentrations, and $D^{\pm}$ the diffusion coefficients, of the cations and the anions, ψ is the electric potential, F the Faraday number, R the universal gas constant, T the absolute temperature, and the distance x is measured in the direction of the flow of the liquid through the membrane. The expression for the ion fluxes in the macrokinetic theory of reverse osmosis is also written in this form.[2-4] Finally, for the production of a steady-state flow potential $\Delta\psi$, the condition $I = 0$ must be satisfied.

Later[3,4] and earlier[2] studies show almost no differences from the macrokinetic viewpoint. The examination of the action of surface forces in Refs.3, 4, and 32, however, raises the theory of reverse osmosis to a qualitatively new level. The authors of Ref.2 took account of a single mechanism for the decrease in the concentration of the ions close to the surface, namely the charge mechanism, due to the presence of the electrical double layer. In Refs.3, 4, 37, and 38, the macrokinetic theory was given a much more general character as a result of the inclusion of the energy of the effective interaction of the ion (or molecule) U with the pore surface. This energy is obviously a function of the distance from the ion to the surface, that is a function of r in the model of a cylindrical capillary (r is the distance to the axis of the capillary). In particular, the dependence of U on r can characterise the energy of electrostatic interaction, so that the theoretical considerations put forward in the pioneering work[2] can be regarded as a particular case of the general theory developed in Refs.3, 4, 37, and 38.

The considerable mathematical difficulties associated with the theory of the non-equilibrium electrical double layer and hence non-equilibrium electrical surface phenomena have been overcome[31,32] by using the principle of local equilibrium and by examining the conditions under which it is possible to neglect the deviations from local equilibrium. The theory of reverse osmosis was developed similarly in Refs.2 and 37–39 for the model of a cylindrical pore. The same approximation has also been extended to surface forces of any character acting on the ions in the pore.[3]

For each transverse cross-section at a sufficient distance from the ends of the capillary, it can be assumed approximately that the distributions of the concentration $C_i(x,r)$ and the energy $U_i(x,r)$ for an ion of the ith kind will be the same as if each section of the capillary were in equilibrium with an electrolyte volume characterised by definite parameters of the thermodynamic equilibrium, different for different sections of the capillary, namely the values of the concentrations of its components $c_i(x)$, the electrostatic potential $\psi(x)$, and the pressure $p(x)$. These parameters should naturally have values intermediate between the corresponding values for the solution on the two sides of the capillary.

Eqns.(7) and (5) for the ion fluxes can be supplemented by the Stokes equation

$$-\operatorname{grad} p-\sum_i C_i \operatorname{grad} U_i+\eta\Delta v=0 \tag{8}$$

where p is the hydrostatic pressure in the capillary, η the viscosity of the liquid, and Δ the Laplace operator.

Inside the capillary, where the force field of its walls is effective, the potential of the average force $f_i(r)$ is variable. As a result, its changes also alter the concentrations of the components of the solution $C_i(r)$ and the pressure $P(r)$. The corresponding distributions can be represented as the sums of their values in the uniform solution c_i and p and the changes Δc_i and π due to the influence of the walls:[3]

$$U_i=\psi+f_i;\quad C_i=c_i+\Delta c_i;\quad P=p+\pi \tag{9}$$

It can be assumed that in a cross-section at a sufficient distance from the ends of the capillary, f_i, Δc_i, and π depend only on r, and not on x. In each cross-section, local equilibrium is preserved, that is the radial fluxes are equal to zero:

$$j_r=0;\quad v_r=0 \tag{10}$$

Integrating Eqns.(7) and (8) with allowance for Eqns.(9) and (10) and using the boundary conditions for $x = 0$, which corresponds to the free electrolyte solution, where

$$f_i=0;\quad c_i=c_0;\quad \pi=0 \tag{11}$$

gives

$$C_i(x,r)=c_i(x)\exp\left(-\frac{f_i}{kT}\right);$$
$$\pi=kT\Sigma\,\Delta c_i=kTc_i(x)\sum_i\left[\exp\left(-\frac{f_i(x,r)}{kT}\right)-1\right] \tag{12}$$

where k is the Boltzmann constant.

After substituting Eqns.(12) in Eqns.(7) and (8), the latter can be represented as linear combinations of the gradients of the parameters of the thermodynamic equilibrium along the direction x:

$$Q=k_{11}\left(-\frac{\mathrm{d}p_0}{\mathrm{d}x}\right)+k_{12}\left(-kT\frac{\mathrm{d}\ln c}{\mathrm{d}x}\right)+k_{13}\left(-\frac{\mathrm{d}\psi}{\mathrm{d}x}\right) \tag{13}$$

$$J_S=k_{21}\left(-\frac{\mathrm{d}p_0}{\mathrm{d}x}\right)+k_{22}\left(-kT\frac{\mathrm{d}\ln c}{\mathrm{d}x}\right)+k_{23}\left(-\frac{\mathrm{d}\psi}{\mathrm{d}x}\right) \tag{14}$$

$$I=k_{31}\left(-\frac{\mathrm{d}p_0}{\mathrm{d}x}\right)+k_{32}\left(-kT\frac{\mathrm{d}\ln c}{\mathrm{d}x}\right)+k_{33}\left(-\frac{\mathrm{d}\psi}{\mathrm{d}x}\right) \tag{15}$$

The coefficients k_{ik} represent integrals whose calculation in accordance with Eqns.(12) requires a knowledge of the concentrations $C_i(x,r)$ in the capillary for equilibrium with a volume solution with concentration $c(x)$. Using the Onsager principle, $k_{21} = k_{12}$, $k_{32} = k_{23}$, and $k_{31} = k_{13}$.

V. THE CHARGE MECHANISM OF REVERSE OSMOSIS

1. Donnan Exclusion of the Ions

The system of equations (13)–(15) was first proposed in Ref.39 for the particular model in which the concentration of the ions in the capillary differs from the bulk concentration only as a consequence of the charged state of the capillary walls, and the potential of the average force is equal to the product of the charge of the ion z_i and the electrostatic potential: $U_i = z_i\psi$. This corresponds to the assumption that the solution in the capillary forms a diffuse electrical double layer, described in the Gouy–Chapman theory by the equation

$$\Delta\Psi=\varkappa^2\operatorname{sh}\Psi, \tag{16}$$

where $\Psi = e\psi/kT$, and the Debye length is given by the expression:

$$\varkappa^{-1}=\left(\frac{\varepsilon kT}{4\pi e^2 c}\right)^{1/2} \tag{17}$$

where e is the charge of the electron, and ε the dielectric constant.

The system of equations (13)–(15) together with the boundary conditions (3) and (11) was solved in Ref.2 using a number of simplifications, which are discussed in Ref.3. In particular, the distribution $\Psi(r)$ for each cross-section of the capillary of radius a was selected to satisfy the boundary condition:

$$\Psi|_{r=a}=\Psi(c_0) \tag{18}$$

This assumption is justified in two limiting cases, when

$$\varkappa a\gg 1 \tag{19}$$

$$\varkappa a\ll 1 \tag{20}$$

When Eqn.(19) applies, the solution of the electrolyte with a composition different from the bulk composition occupies only a small

region of the capillary next to the wall. Thus $c(x)$ differs little from c_0, and the selectivity of the membrane is correspondingly low. When Eqn.(20) applies, the potential $\psi(r)$ and hence f_i change little in the transverse cross-section of the capillary. In this case, however, ψ is almost the same for all cross-sections of the capillary, so that the simplification (18) is justified.

In Ref.3, the system of equations (13)–(15) was solved over a wide range of values of κa both with the boundary condition (18) and assuming that the charge density on the capillary surface is constant:

$$\sigma_0 = -\varepsilon \frac{d\Psi}{dr}\Big|_{r=a} = \text{const} \qquad (21)$$

It was found that the selection of the conditions for a constant charge or a constant potential has little influence on the selectivity, that is the indeterminancy associated with the usually insufficient knowledge of the mechanism of production of the double layer has no significant influence on the predictive power of the theory. In Ref.2, good agreement was obtained between theoretical and experimental data on the dependence of the selectivity on various parameters (the Debye radius, the Peclet number, and the surface potential).

Similar results were obtained for colloidal membranes.[40] A large amount of evidence for the decisive role of the surface charge has been obtained in the study of the selectivity of dynamic membranes formed from colloidal particles[41] and polyelectrolytes.[42] Although the desalinating action of cellulose acetate membranes is not determined by the charge mechanism, in the range of low concentrations this mechanism also makes a definite contribution to the selectivity in this case.[43] This was reflected in Ref.44, where the dependence of the selectivity of these membranes on the pH of the solution was described by an extremal curve with a minimum lying at the pH which ensured that the charge of the membrane was equal to zero. Since the contribution of the charge mechanism for symmetrical electrolytes is independent of the sign of the charge of the membrane, the selectivity when the charge is equal to zero should pass through a minimum. Thus the results obtained in Ref.44 shows fairly convincingly that the charge mechanism also operates in cellulose acetate membranes.

The possibility of using charged membranes with wide pores in reverse osmosis is indicated by the results obtained in Ref.45, where it was found that even the cellulose acetate ultra-filtration membranes UAM-100, in spite of the extremely low density of the surface charge of the cellulose acetate and the large pore dimensions, retain some selectivity up to an electrolyte concentration of 10^{-2} M, reaching a maximum selectivity $\varphi = 0.6-0.65$ at the minimum concentration studied, 10^{-4} M.

For high Peclet numbers, the electrolyte concentration remains practically constant and equal to c_0 along practically the entire thickness of the dividing layer (a rapid decrease in concentration takes place close to the boundary of the dividing layer and the wide-pore layer of the membrane), and the charge mechanism of reverse osmosis is revealed extremely clearly. In the case of high selectivity, which is of the greatest practical importance, the corresponding expression for the selectivity of the membrane acquires a simple form when condition (20) is satisfied.

There is a definite similarity between the charged dividing layer of an asymmetric reverse-osmosis membrane and the ion-exchange membrane used in electrodialysis. This membrane is not directly applicable for reverse osmosis, because of its large thickness and corresponding high hydrodynamic resistance. The main electrochemical regular features in the ion-exchange membrane–electrolyte system also apply, however, to the charged dividing layer of an asymmetric membrane.[46]

These regular features are: a) the shielding of the electric field of the ion by the charge of opposite sign at distances greater than the Debye length; b) the local electrical neutrality of the homogeneous phases at distances from the phase interface greater than the shielding length, and the integral electrical neutrality of the heterogeneous system as a whole; and c) the constant electrochemical potential within the heterogeneous system, that is the equality of the electrochemical potentials in the resin and electrolyte phases. Local electrical neutrality is understood to indicate that the algebraic sum of the charges of the ions is equal to zero within each physically infinitely small volume.[46] This definition will be used in the examination of the ratio of the concentrations of the mobile cations and anions in the ion-exchange membrane.

The matrix of ion-exchange membranes contains ionogenic groups, which on contact with the solvent dissociate to give a charge fixed by the surface.[50] The ions of an electrolyte whose sign is the opposite of the sign of the surface charge of the membrane are usually called counter-ions, and the ions with the same charge are called co-ions. The membrane phase must contain sufficient counter-ions to compensate the surface charge. These counter-ions are described as being exchange sorbed. Moreover, in accordance with the third of the above conditions (constant electrochemical potential), the membrane phase must also contain some co-ions. In other words, since the co-ions are in the electrolyte, they must also be present in the membrane, but at a different concentration. Since the membrane and the co-ions have charges of the same sign, the concentration of the latter in the membrane phase is lowered. It is also clear that the membrane should also contain counter-ions which in turn compensate the charge of the co-ions present. These co-ions and counter-ions are usually described as the non-exchange sorbed electrolyte. It follows that the concentration of non-exchange sorbed electrolyte in the membrane phase is lower than the concentration of the equilibrium solution. This phenomenon is called Donnan exclusion of the electrolyte from the ion-exchange membrane phase.[46–48]

In accordance with the electrical neutrality condition, the exchange sorbed counter-ions cannot leave the membrane phase, since they compensate the surface charge. Only the non-exchange sorbed electrolyte can leave the membrane; the filtrate is therefore desalinated relative to the solution being separated.

The concentration of co-ions in the membrane is lower, the larger the Donnan electric potential jump Ψ_D.[46,48] This equilibrium potential jump is produced as a consequence of the removal of some of the counter-ions from the membrane layer next to the surface into the electrolyte, as a result of which a volume charge is produced in the electrolyte layer next to the surface due to the excess of counter-ions; a volume charge of opposite sign is produced simultaneously in the membrane layer next to the surface Some of the counter-ions leave the membrane, since their concentration in the highly charged membrane is higher than that in the surrounding electrolyte. The lowered concentration of co-ions in the membrane is described in terms of the Donnan potential using the familiar Boltzmann equation.

The Donnan potential is greater, the greater the exchange capacity or the corresponding concentration of surface charges in the volume of the membrane c_f and the lower the electrolyte concentration. These qualitative relationships are confirmed by a quantitative

analysis, which leads, on the basis of a quantitative examination of the third and fourth conditions, to an expression which describes the Donnan potential and hence, using the Boltzmann equation, the concentration of co-ions in the membrane:[46–48]

$$c^{co} = \frac{1}{2}[(c_f^2 + 4c_0^2)^{1/2} - c_f] \quad (22)$$

In the case of low electrolyte concentrations, which is of the greatest interest, when

$$c_0 \ll c_f \quad (23)$$

this equation is simplified to:

$$c^{co} \simeq c_0^2/c_f \quad (24)$$

This leads to the following expression for the selectivity:

$$\varphi = \left(1 - \frac{c^{co}}{c_0}\right) = \left(1 - \frac{c_0}{c_f}\right) \quad (25)$$

from which it follows that the selectivity may approach 1 with decrease in the electrolyte concentration, when condition (23) begins to be satisfied.

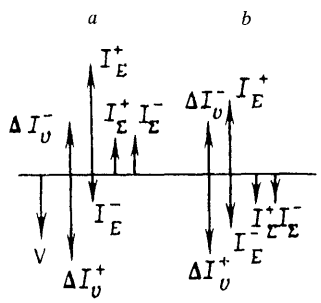


Figure 1. Influence of the transport numbers of the ions on the selectivity of the membrane.

Eqn.(25) can give a value of the selectivity which is too high, since it does not take account of the fact that the polarisation field, at the same time as retarding the counter-ions, increases the transport of co-ions through the membrane. If it is assumed that the membrane is negatively charged, the convective flux of counter-ions I_v^+ will be greater, and that of the negative ions I_v^- will be less, than if the liquid passed through a capillary, preserving the original concentration, when $I_{v0}^+ = I_{v0}^-$. In Fig.1, the corresponding arrows show the magnitude and direction of the excess convective fluxes $\Delta I_v^\pm = I_v^\pm - I_{v0}^\pm$. The distance between the ends of the arrows for ΔI_v^+ and ΔI_v^- gives the magnitude of the electric current due to the convective flux of the ions (the so-called flow current). The arrows $I_E^\pm$ characterise the ion fluxes produced under the influence of the polarisation electric field. The condition that the electric current through the membrane be equal to zero is satisfied if the distance between the ends of the arrows ΔI_v^+ and ΔI_v^- is equal to the distance between the ends of the arrows I_E^+ and I_E^-. The resulting excess fluxes of the cations I_Σ^+ and anions I_Σ^- are the same, and equal to the excess flux of the salt.

Desalination takes place when the excess flux of the salt and the flow of liquid take place in opposite directions. Fig.1*a* shows that this situation obtains if

$$I_E^+/I_E^- = a_E^+/a_E^- > \Delta I_v^+/\Delta I_v^- \quad (26)$$

where $a_E^\pm$ represents the so-called transport numbers, defining the fraction of the total current carried by the cations and the anions respectively when a potential difference is applied to the membrane in the absence of other thermodynamic forces. If the opposite inequality is satisfied (Fig.1*b*), filtration through the membrane leads to concentration of the salt. The passage of the counter-ions close to the fixed charges of the membrane may be retarded by electrostatic forces of attraction, so that $a_E^- > a_E^+$. If the fixed charges are hydrated, the distance of closest approach increases, and the electro-static attraction becomes weaker, so that the hydrophilic character of the membrane helps to satisfy condition (26).

Information on other studies of the charge mechanism is given in a detailed review.[44] The data given more or less agree with the above conclusions.

2. Asymmetric Charged Membranes as a Basis for the Creation of a Technology for the Desalination of Slightly Mineralised Water Using Low-Pressure Reverse Osmosis

The extensive introduction of reverse osmosis is being retarded, firstly, by the complexity of the equipment, and, secondly, by the low intensity of the mass exchange processes.[1,7] The first difficulty is to a large extent due to the need to use high pressures, which is unavoidable in the demineralisation of salt water, since in this case it is necessary to overcome a high difference in osmotic pressure.

In the demineralisation of brackish water, however, and in particular in desalination technology, the osmotic pressure drop is much smaller. For the requirements of power engineering and the electronics industry and for the demineralisation of brackish water, it is possible in principle to create a technology of reverse osmosis using moderate pressures. The equipment for reverse osmosis at pressures of ~10 atm is much simpler. When the membranes of the MGA series used at present are employed, however, an appreciable decrease in pressure would lead to an unacceptably large decrease in efficiency. It is appropriate to use these and similar membranes, which retain the required selectivity at high salt concentrations (as a result of the very small pore dimensions), for the demineralisation of salt water. Their use to treat weakly mineralised water is not the optimum technological solution, however. Up to the present, the synthesis of membranes has been aimed at ensuring the optimum geometric characteristics (pore dimensions, porosity, thickness of the active layer), and insufficient attention has been paid to colloid–electrochemical methods for intensifying selective membrane transport. Neglect of the role of the membrane charge is probably justified in the technology of the demineralisation of salt water. With decrease in the salt concentration, however, the conditions for demineralisation by reverse osmosis change radically.

The technology of the low-pressure reverse osmosis of slightly mineralised water should be based on asymmetric relatively wide-pore membranes with the optimum charge.

The reverse-osmosis membranes used at present are very weakly charged.[49–53] The idea that the introduction into the membrane matrix of a fixed surface charge might make the active layer looser

(as a result of the electrostatic repulsion of the charges on the surface of the pores) and hence make the membrane more efficient while preserving its high selectivity as a result of the long-range action of the electrostatic forces was first put forward in Ref.54. Since then, about a dozen papers have described attempts to synthesise and study the properties of charged reverse-osmosis membranes. The most interesting studies are those described in Refs.55 and 56. The first describes a method for obtaining membranes by sulphonating or aminating a polystyrene–butadiene resin. These membranes had a fairly high selectivity (95–98%) at low concentrations, but their efficiency was low (0.1–5 litre m^{-2} d^{-1} $atom^{-1}$) due to the large thickness of the membrane (500 μm) and its symmetrical structure. It might be possible to use this method to synthesise much thinner membranes with a high efficiency.

Another method for obtaining highly efficient membranes[56] involves the deposition and subsequent grafting of a thin layer of a polyelectrolyte on the surface of an ultra-filtration membrane. This method has been used to obtain thin-layer composite membranes with a very high efficiency (30–150 litre m^{-2} d^{-1} atm^{-1}). The selectivity was low, however (60% with respect to singly-charged anions). The authors of Refs.55 and 56 (and of other similar studies, for example Refs.57 and 58) apparently did not conclude that the most appropriate field of application of charged membranes is with fairly dilute solutions. The lack of understanding of the fact that the average concentration of co-ions along the cross-section of the pores in charged membranes can be lowered considerably has prevented a full evaluation of the advantages of charged reverse-osmosis membranes, so that work devoted to their development and study is still fairly fragmentary. Systematic work on the synthesis, study, and use in desalination of asymmetric charged membranes is therefore necessary.

VI. THE SELECTIVITY OF NON-CHARGED MEMBRANES AND THE STANDARD CHEMICAL POTENTIALS OF IONS

The lowered concentration of a salt in non-charged membranes leads to a decrease in the value of the standard chemical potential (SCP) of the ion in the pores of the membrane, due to the interaction of the ion with the polymeric dielectric matrix of the membrane or to the change in the structure of water in it.[59] A quantitative characteristic of this effect is provided by the distribution coefficient, that is the ratio of the average concentrations of the ions in the membrane phase c_m and in the bulk of the electrolyte:

$$\gamma = \bar{c}_m / c_0 \tag{27}$$

This characteristic, which is extremely important for reverse osmosis, is readily expressed in terms of the SCP, taking into account the condition for electrochemical equilibrium in the membrane–electrolyte system for both the cations and the anions, $\mu_e^{\pm} = \mu_m^{\pm}$, where $\mu_e^{\pm}$ and $\mu_m^{\pm}$ are the electrochemical potentials of the ions in the electrolyte and membrane phases respectively.

When the familiar expression for the electrochemical potential of an ion in a dilute electrolyte is used, these equations acquire the form:

$$\mu_{m0}^{\pm} \pm e\psi_m + kT \ln c_m^{\pm} = \mu_{e0}^{\pm} \pm e\psi_e + kT \ln c_0^{\pm} \tag{28}$$

where $\mu_{m0}^{\pm}$ and $\mu_{e0}^{\pm}$ are the standard chemical potentials of the ions in the membrane and electrolyte phases respectively. Eliminating the interphase potential jump from these equations and making use of the condition for local electrical neutrality in the membrane and electrolyte phases gives:

$$c_m = c_0 \exp\left[\frac{\mu_{e0}^{+} - \mu_{m0}^{+} + \mu_{e0}^{-} - \mu_{m0}^{-}}{2kT}\right] \tag{29}$$

Since in the non-charged membrane the concentrations of the cations and the anions are equal, a flow potential and hence electromigration fluxes of the ions are not produced. At high Peclet numbers, the diffusion fluxes are also unimportant. This means, however, that the salt concentration in the filtrate c_2 coincides with the salt concentration in the membrane c_m. This makes it possible to make the equation for the selectivity more specific:

$$\varphi = 1 - \gamma = 1 - \exp\left[\frac{\mu_{e0}^{+} - \mu_{m0}^{+} + \mu_{e0}^{-} - \mu_{m0}^{-}}{2kT}\right] \tag{30}$$

where γ is defined by Eqn.(27).

VII. THE DIELECTRIC EXCLUSION OF IONS FROM MEMBRANE PORES

1. Image Forces

A decisive role in the mechanism of the dielectric exclusion of ions from the pores of a membrane is played by the interaction of the ion with the polarisation charges,[60–64] which are produced at the interface between media characterised by different dielectric constants (DC). Since for a single planar interface the interaction of an ion with this interface can be described formally as an interaction with a fictitious charge or image, the phenomenon being considered is usually described as the production of "image forces". These forces play an important role in many electrochemical systems.[65]

It is possible to consider first the limiting case of an isolated ion, that is to assume that the shielding length is so much greater than the characteristic pore dimensions that the shielding can be neglected. Since the DC of the membrane matrix ε_m is lower than the DC of the solvent ε, the sign of the polarisation charges on the surface of the pores coincides with the sign of the charge on the ion. The repulsion between like charges leads to an increase in the SCP of the ion, which in accordance with the condition of constant electrochemical potentials leads to a decrease in the electrolyte concentration in the pores.

In the case of a charged membrane, only the concentration of the co-ions is lowered, and the concentration of the counter-ions is increased, whereas in the pores of a non-charged dielectric membrane the concentrations of both the cations and the anions are lowered (the concept of co-ion and counter-ion in this case is obviously meaningless); in the case of a binary symmetrical electrolyte, their excess SCP are approximately equal.

From the obvious fact that the rate of flow of the liquid and the concentration of the electrolyte have maximum values in the central part of the pore, it follows that the main contribution to the salt flux is made in this region. The results of calculations for the case of a flat capillary[66] confirm this qualitative conclusion and show that the salt flux can be estimated with a relative uncertainty of not more than 20–30%, from a knowledge of only the concentration in the central part of the pore.

The dependence of the intensity of dielectric exclusion on the geometry of the pore space is of considerable interest. When there is no shielding in the system, there is only one characteristic length, namely the pore dimensions. By changing to dimensionless

coordinates in the equations, it can be shown that in all cases the excess SCP due to the image forces W is inversely proportional to the pore dimensions. Moreover, it is always directly proportional to the square of the charge of the ion $q = ez$ and inversely proportional to the DC of the solvent. Thus irrespective of the shape of the pore, it is possible in the expression for the excess SCP of the ion to distinguish the factor $2W\varepsilon R/q^2$, and the remaining factor depends on the ratio of the DC of the matrix to that of the solvent, $\beta = \varepsilon_m/\varepsilon$.

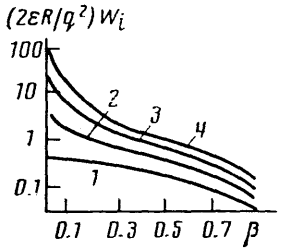


Figure 2. Dependence of the intensity of the dielectric exclusion on the geometry of the pore space:[64] *1*) ion close to a plane, *2*) planar gap, *3*) cylinder, *4*) sphere.

Fig.2 gives the dependence of $2W\varepsilon R/q^2$ on the parameter β for four cases, where the ion is situated: 1) at a distance R from a planar interface, 2) in the middle of a planar gap with a width of $2R$, 3) on the axis of a cylindrical capillary with a radius R, and 4) at the centre of a spherical cavity with a radius R.[64] A noteworthy feature is the very strong dependence of the intensity of dielectric exclusion on the geometry of the system, particularly at low values of β.

The physical significance of this dependence is that, as is well known, the density of the energy of the electric field is inversely proportional to the DC of the medium. It is for this reason that the standard chemical potential of an ion increases close to bodies with a lower DC. When a medium shows dielectric non-uniformity, the lines of force of the electric field are deformed. In this connection, the extent to which the geometry of the pore space is closed is very important; this determines the possibility that the lines of force of the field "by-pass" the regions with lower DC. For example, in the case of a single planar interface there is an entire half-space with an increased DC. In this case the energy of the "image forces" is low. At the same time, for the limiting closed geometry of a sphere, all the lines of force penetrate the medium with the low DC, so that the magnitude of W is a maximum in this case.

A spherical pore is of interest only as an example of limiting closed geometry, since flow of a liquid is impossible in it. It may be noted that the curves corresponding to the geometries of a sphere and a cylinder lie not far from one another (Fig.2), and the intensity of dielectric exclusion is also fairly high in the latter case. For example, the selectivity of a cylindrical capillary with a diameter of 3 nm ($\varepsilon_m = 3$, $\varepsilon = 80$) is ~ 0.9. Decrease in the pore dimensions evidently leads to a sharp increase in the selectivity. Thus in the case of the dielectric exclusion mechanism, membranes with cylindrical pores should "function" most effectively.

The dielectric exclusion of ions in real membranes can be reduced approximately to the solution of the electrostatic problem of an ion in a right cylindrical capillary. The membrane selectivity due to this mechanism is high, even if the pore size is much greater than the size of the ion.

The interaction of the separated ion with the polarisation charges is complicated by the presence of other ions in the pore. In the pore, each ion is surrounded by an atmosphere of counter-ions, as in the free solution. If the Debye radius is smaller than the pore radius, then the electric field of an ion situated at the centre of the pore does not in practice reach the pore surface and does not polarise it, so that the image forces are weak. A quantitative theory of this effect of shielding of the image forces has been developed using the model of a flat capillary. In this case it is possible to obtain a very simple approximate equation for the excess SCP of an ion situated on the axis of the capillary:[67,68]

$$W = \frac{-q^2}{2\varepsilon R} \ln [1 - \alpha \exp(-2\varkappa_i R)] \qquad (31)$$

where

$$\alpha = (\varepsilon - \varepsilon_m)/(\varepsilon + \varepsilon_m);$$

and $\varkappa_i^{-1}$ is the shielding length inside the pores.

Since as already noted in the case of dielectric exclusion the concentration of the ions of both signs in the pores is lowered, the "internal" shielding length is greater than the "external" length (that is the shielding length in the bulk of the equilibrium solution). Thus an increase in the selectivity of the membrane in this case leads to a decrease in the shielding effect, whereas an increase in the density of the fixed charge of ion-exchange membranes, which is accompanied by an increase in their selectivity, leads to the opposite effect.

Another interesting characteristic of Eqn.(31) is that when $\alpha < 1$, the decrease in the magnitude of W begins not at $\varkappa_i R \simeq 1$ but at $\varkappa_i R \simeq 0.2$. This is due to the fact that in the absence of shielding a large contribution to the SCP of the ion is made by so-called "multiple images". In other words, this phenomenon can be described as mutual polarisation of the surfaces; as a result, the polarisation charge as it were extends along the surface to distances which are much greater than the width of the capillary. The shielding of the interactions with it therefore naturally begins at $\varkappa_i R < 1$.

Fig.3 shows the theoretically calculated concentration dependence of the excess SCP of ions situated in flat capillaries with different widths.[68] It can be seen that the smaller the width of the pores of the membrane, the higher the concentration at which the decrease in selectivity begins. This corresponds completely with what has been said above. It should be noted, however, that even in the case of highly selective membranes, the decrease in selectivity takes place at concentrations which are not very high. This conclusion does not fully agree with experiment. Here, it is helpful to introduce the concept of non-local dielectric shielding in polar media,[69-71] which takes account of the fact that dipole shielding, like ion shielding, is fully developed only at distances greater than the correlation length (for ion shielding this is the Debye length). For water, these distances have been estimated[69] as 0.5–0.7 nm, that is they are commensurate with the dimensions of fine pores.

Strictly speaking, the interaction of an ion with polarisation charges is influenced not only by ionic shielding but also by dielectric shielding. In the local approach used up to the present, this feature is taken into account by dividing the quantity W by the static DC of the solvent. If account is taken of the non-local character of the dielectric response, it may be concluded that the DC

close to the ion is effectively lowered (since at small distances the bound charge cannot be completely formed); the interaction with the polarisation charges separated on the surface therefore increases. This leads, firstly, to a considerable intensification of the dielectric exclusion, and, secondly, to a change in the ratio of the relative contributions of single and multiple images in the excess SCP of the ions in favour of the former. The explanation for this is that the correlation length cannot be much larger than the pore dimensions; thus only the interaction with the first images experiences weak dielectric shielding, and the interaction with the other images takes place in practically the same way as in a medium with a static DC. In this situation, ionic shielding as far as $\kappa_i R \simeq 1$ should lead to a decrease in the already small contribution of the multiple images, and a significant decrease in the intensity of dielectric exclusion begins at $\kappa_i R \gtrsim 1$.

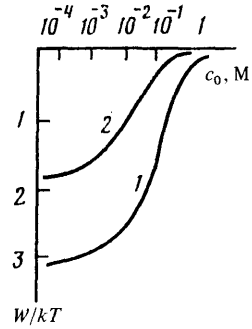


Figure 3. Concentration dependence of the SCP of ions for a model of membranes with a pore half-width of 0.3 nm (*1*) and 0.5 nm (*2*).[68]

2. The Combined Effect of the Dielectric and Charge Mechanisms

In moderately wide charged pores, the simultaneous operation of the charge and dielectric mechanisms leads to a decrease in the concentration of co-ions. If it is assumed that these effects are additive, the distribution coefficient of the co-ions is given by the equation:

$$\gamma = \frac{c^+}{c_0} = \exp\left[\frac{-e\psi + W}{kT}\right] \qquad (32)$$

The equation used to find the Donnan potential now contains the SCP, which depends on the image forces:

$$\operatorname{sh}\frac{e\psi}{kT} = \frac{c_f}{2c_0}\exp(W/kT) \qquad (33)$$

Simplifying this equation for the case of greatest interest, that of high values of the Donnan potential and substituting the result in Eqn.(32) gives

$$\gamma = \frac{c_0}{c_f}\cdot\exp(-2W/kT) \qquad (34)$$

and it can be seen that in this case there is not simple multiplication of the Donnan and dielectric factors but a quadratic increase in the intensity of dielectric exclusion.

Increase in the fixed charge, however, leads to an increase in the concentration of counter-ions, so that the shielding influence is increased. As a result, the effects of dielectric exclusion in the case of highly charged ion-exchange membranes apparently are not very significant. Membranes having a moderate charge are more promising for the combination of the effects of these two mechanisms. This leads to the practical conclusion that it is appropriate to give membranes a surface charge not only for desalination but also for the demineralisation of so-called brackish water with a higher concentration.

VIII. THE HYDROPHILIC CHARACTER OF MEMBRANES AND REVERSE OSMOSIS

In addition to the electrochemical mechanisms examined above (the Donnan and dielectric exclusion of ions), another factor leading to a decrease in the concentration of the dissolved substance in sufficiently fine pores of membranes is the change in the structure of water.[72,73] This is confirmed by the fact that hydrophilic reverse osmosis membranes effectively retard not only an electrolyte but also the neutral molecules of substances such as sugar, alcohol, and acetone.

The change in the solvent power of the pore water of hydrophilic membranes with respect to ions is due to a number of factors.[59,74] One of the results of the change in the structure of water is a lowering of its dielectric constant. The intrinsic energy of an ion in the membrane pores, calculated, for example, by the Born method, is then found to be higher than that in the free solution,[75] leading to a decrease in the concentration of the ions in the membrane pores. The Born approximation may be inadequate, however, since the mechanism of the phenomenon being considered may in fact be much more complex.[76,77]

Since there is no theoretical justification for the influence of the hydrophilic character of membranes on their selectivity, the results of some recent experiments are of particular interest. The experiments were carried out using three membranes of different hydrophilic character.[78] The most hydrophilic was a composite polyamide membrane (*A*), obtained by interphase polycondensation.[79] The other two reverse-osmosis membranes were prepared from homopolymers based on polyhydroxydiazole (*B*) and the even more hydrophobic polycarbonate (*C*). For this series of membranes, the selectivity coefficients were measured for alkali metal chloride solutions with different concentrations c_0. The highest selectivity was observed for the most hydrophilic membrane *A* (Fig.4).

The preservation of a high selectivity over a wide range of electrolyte solution concentrations (as far as 0.5–1 M) is a distinguishing feature of hydrophilic membranes. Nevertheless, their selectivity decreases with increase in the concentration of the solutions. This is due to the breakdown of the characteristic structure of water in the fine pores and the gradual approach of the structure of the solution to that in the bulk. The breakdown takes place as a result of the influence of the ions on the structure of water, which increases with increasing concentration of the solution; this increasing influence suppresses and then exceeds the influence of the hydrophilic surface of the pores.

It is natural to expect that ions which have a stronger influence on the structure of water should bring about a greater decrease in the selectivity with change in concentration. Thus Li^+ ions, which have the smallest radius and the highest hydration numbers, in all cases (Fig.4) bring about a sharper decrease in the selectivity

coefficient. On the other hand, Cs^+ ions, which have the largest radius and small hydration numbers, have less influence on the structure of water in the pores, leading to preservation of the high selectivity of the membrane and its weaker dependence on the concentration of the solution.

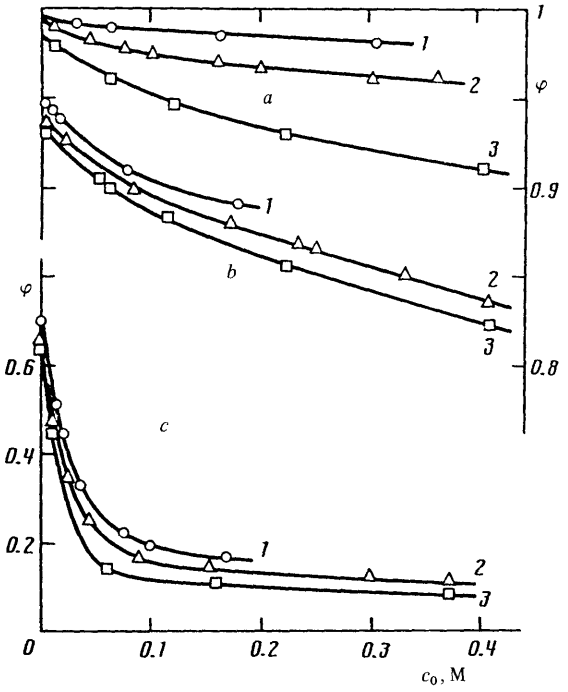


Figure 4. Dependence of the selectivity coefficient φ on the concentration of solutions of the electrolytes CsCl (*1*), KCl and NaCl (*2*), and LiCl (*3*) for membranes with different hydrophilic character.[78]

IX. THE MACROKINETIC THEORY OF REVERSE OSMOSIS AND THE PHYSICAL MODELLING OF MEMBRANES

It can be seen from the foregoing that calculations at the molecular level at present make it possible to determine only the equilibrium distributions of the components in the pores of a membrane. Even in this case, however, a purely theoretical approach to specific membranes is impossible, since, firstly, the size distribution of the pores is unknown, and, secondly, it is impossible to take account of the change in the structure of water, a factor which cannot yet be calculated quantitatively.

This makes it necessary to carry out a range of experimental measurements and compare the results with the results of a calculation of the kinetic coefficients using the system of equations of macrokinetic theory. A system of equations of this kind[80] has been used to develop a set of required measurements. The general formulation of the problem, given in section IV, was simplied in Ref.80 by introducing the boundary condition (20). This made it possible to calculate the kinetic coefficients and to obtain equations for the selectivity φ and the flow potential $\Delta\psi$:

$$\varphi = 1 - \frac{\exp(\mathrm{Pe}/k_1)}{1 - k_2 + k_2 \cdot \exp(\mathrm{Pe}/k_1)} \tag{35}$$

$$\Delta\psi = FR_m\bar{c}_0 Q - \frac{RT}{F}(a_E^+ - a_E^-)\frac{\bar{c}_s}{2c_0} \tag{36}$$

where

$$\frac{\mathrm{Pe}}{k_1} = \frac{1}{4}\frac{F^2}{RT}\cdot\frac{[\bar{c}_s - (a_E^+ - a_E^-)\bar{c}_0]QR_m}{a_E^+ a_E^-};\quad k_2 = \left[\frac{\bar{c}_s}{2c_0} - (a_E^+ - a_E^-)\frac{\bar{c}_0}{2c_0}\right]$$

$\bar{c}_s = \bar{c}^+ + \bar{c}^-$, $\bar{c}_0 = \bar{c}^+ - \bar{c}^-$ are the average concentrations of the cations and the anions in the hydrodynamically mobile part of the pore space (with a statistical weight corresponding to the distribution of the rates in viscous flow); and R_m is the electrical resistance per unit surface area of the membrane.

To determine c_0 and c_s it is sufficient to measure the following parameters by the usual methods: 1) the selectivity coefficient φ, 2) the membrane potential difference $\Delta\psi$, 3) the resistance of the membranes R_m, and 4) the transport numbers $a_E^{\pm}$. This set of measurements can give information on two of the most important characteristics of the mechanism of reverse osmosis, namely the Donnan potential (see part 1 of section IV) and the differences in the standard chemical potentials of the ions (section V). The introduction of this set of measurements in laboratories working on the theory and technology of reverse osmosis will make it possible to check different versions of the theory of reverse osmosis. A physical model of the membrane should be constructed in each specific case; this will lead to optimisation of the conditions for reverse osmosis and indicate methods for improving the quality of membranes.

X. A GENERALISED MATHEMATICAL MODEL OF THE REVERSE OSMOSIS OF ELECTROLYTES

The most general mathematical model of the processes of reverse osmosis,[4,81] which can be regarded as a further generalisation of the conclusions in Refs.3 and 37, has recently been developed. The generalisation was achieved by taking simultaneous account of membrane transport and external-diffusion kinetics, the charge and non-charge mechanisms of the exclusion of ions from the membrane pores, and the extension of the theory to unsymmetrical electrolytes and electrolyte mixtures. This has made it possible to obtain a number of results of practical importance.

The combined description of convective diffusion within a membrane and in the concentration polarisation layer involves two dimensionless Peclet numbers, one internal [Eqn.(4)], and one external, Pe_0. When

$$\mathrm{Pe}_0 = mv\delta/D \ll 1 \tag{37}$$

(where m is the porosity of the membrane, and D the diffusion coefficient in the bulk solution), concentration polarisation does not lower the selectivity of the membrane. At low flow rates v, this condition is fulfilled, but condition (4) is not. With increase in the rate, however, condition (4) begins to be satisfied, but condition (37) is no longer satisfied. Thus the theory[4,81] predicts a maximum on the curve giving the dependence of the selectivity of the membrane on the flow rate, corresponding to optimum separation conditions (curve *1* in Fig.5). The calculations were carried out for the following conditions: $\gamma_- = 10^{-2}$, $\gamma_+ = 0.1$ (which corresponds to the preferential introduction of cations into the pores), and $2h/m\delta = 1.5$. The value of the last parameter was selected for those

conditions of mixing of the solution being separated for which, for a membrane with a porosity $m = 0.2$, the thickness of the non-mixed layer δ is approximately seven times the thickness of the dividing layer of the membrane h.

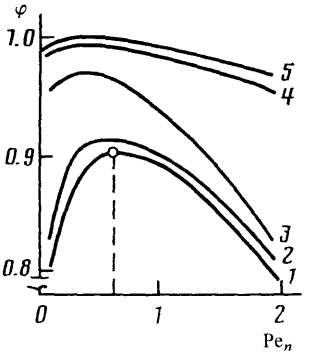


Figure 5. Dependence of the selectivity coefficient φ on the external Peclet number for different surface charges of the membrane σ: *1*) 0; *2*) 0.01; *3*) 0.1; *4*) 1; *5*) 5.[80]

From the general solutions obtained[37,38] it follows that the maximum value of the selectivity $\varphi_{max} = 1-\gamma$ is achieved for $Pe/Pe_0 \geqslant 5$. For a binary electrolyte solution

$$\gamma = \gamma_+^{z_-/z} \cdot \gamma_-^{z_+/z} \qquad (38)$$

where $z = z_+ + z_-$; z_- and z_+ are the valences of the anions and the cations.[81]

The surface charge of a membrane $\sigma = c_f/c_0$ increases its selectivity (curves *2*–*5*). For cellulose acetate membranes, the magnitude of the dimensionless charge at $c_0 = 10^{-2}$ M is $\sigma = 0.1$ (curve *3*), increasing to 1 at $c_0 = 10^{-3}$ M (curve *4*). Thus the influence of the surface charge is greater, the lower the concentration of the electrolyte solution being separated. Thus at $c_0 \geqslant 0.1$ M, the influence of the charge ($\sigma \leqslant 0.01$) is vanishingly small (curve *2*).

For an unsymmetrical electrolyte, a solution can be obtained without taking account of the influence of concentration polarisation, that is by assuming that $Pe_0 \ll 1$. Fig.6 shows the dependence of the selectivity of the membrane on the dimensionless surface charge $\Delta = \sigma/z_+z_-$ (for a 1–1 electrolyte, $\Delta = \sigma$). For $\Delta = 0$, the selectivity of the membrane was taken as equal to $\varphi_{max} = 0.9$. For the unsymmetrical electrolytes $BaCl_2$ (curves *1* and *2*) and $LaCl_3$ (curves *3* and *4*), the selectivity depends on the sign of the charge of the membrane pore surface Δ. Here, curves *1* and *3* correspond to $\Delta > 0$, and curves *2* and *4* to $\Delta < 0$. The efficiency of the retardation of the solution is much greater when the sign of the charge of the multiply-charged ion is the same as the sign of the charge of the membrane. This is because the surface charge has a stronger influence on the more highly charged ion. Thus for $BaCl_2$ and $LaCl_3$, a higher selectivity is achieved when the membrane has a positive charge. On the other hand, for the effective separation of, for example, Na_2SO_4 solutions, it is appropriate to use negatively charged membranes, in agreement with experiment.

Since the values of Δ depend on c_0, the graphs in Fig.6 also reflect the influence of the electrolyte concentration for a fixed membrane charge ($c_f = 5 \times 10^{-3}$ M). The corresponding values of $c_0 = c_f/z_+z_-\Delta$ are given on the upper scale of the abscissa. Fig.6 shows that decrease in the electrolyte concentration leads to an increase in the selectivity of the membrane, due to its surface charge. The same situation is observed for the symmetrical binary electrolyte KCl (curve *5*), but since the charges of the ions have the same value, the sign of the surface charge in this case does not influence the selectivity.

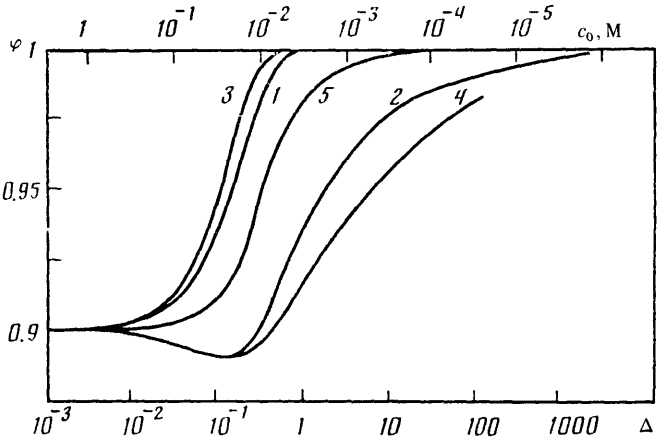


Figure 6. Dependence of the selectivity of a reverse-osmosis membrane on the dimensionless surface charge Δ and on the concentration c_0 of the solutions being separated: *1,2*) $BaCl_2$, *3,4*) $LaCl_3$, *5*) KCl.

The macrokinetic theory examined above for binary solutions[81] has been generalised[82–84] for the case of multicomponent electrolyte solutions. In contrast to the case of binary solutions, in this case the separation involves a change in not only the concentration but also the composition of the solutions. In contrast to the case of binary solutions, in this case the separation involves a change in not only the concentration but also the composition of the solution. The components of the mixture have a mutual influence on one another, whose mechanism is determined by the dependence of the membrane potential $\Delta\psi$ on the composition of the electrolyte solution and the distribution coefficient γ_i for each ion.

This brief review of the present state of the theory of the reverse-osmosis separation of electrolyte solutions shows the great variety of physicochemical factors responsible for the selective action of membranes. Corresponding methods for calculating the selectivity can be developed for each of the retention mechanisms. In real membranes, however, the surface charge, the dielectric exclusion of ions, and the change in the properties of water in the fine pores may exert their influence simultaneously. It is difficult to determine *a priori* the extent of their influence, particularly since there are insufficient data on the structure of the pore space in membranes and on the localisation of the charges and active centres on the surface of the pores and in the bulk of the membrane, which influence both the properties of water and the distribution of ions in

the pore solution. Information on the contribution of a particular mechanism of selectivity can now be obtained by carrying out comprehensive studies of membranes using the procedure developed.[80]

The main qualitative conclusions from the above examination are that for the separation of electrolyte solutions with a low concentration it is necessary to use membranes with a high surface charge, and for the separation of solutions with a higher concentration it is necessary to use membranes whose pore surface is highly hydrophilic. By giving membranes these new properties, it is possible, while retaining fairly high selectivity values, to increase slightly the pore dimensions, and this makes it possible to increase the efficiency or to decrease the expenditure of energy used to pump the solution through the membrane, by using smaller pressure differences.

This also leads to the conclusion that for the separation of solutions with different compositions and concentrations it is necessary to prepare membranes of different types, differing not only in the pore dimensions, as is the case at present, but also in their surface electrical properties and hydrophilic properties.

The main task, whose solution requires the use of the methods of the statistical mechanics of molecular systems and numerical and physicochemical experimental methods, is the refinement of the calculation of the changes in the intrinsic energy of ions in fine pores and the characteristics of the structural state of water. This will make it possible to refine and predict quantitatively the values of the equilibrium distribution coefficients which at present appear as a parameter in the equations of the theory of reverse osmosis.

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