

DESALINATION BY PRESSURE OSMOSIS

U. MERTEN

*General Atomic Division of General Dynamics Corporation,
John Jay Hopkins Laboratory for Pure and Applied Science, San Diego, Calif. (U.S.A)*

(Received June 20, 1966)

SUMMARY

Reverse osmosis is generally thought of as a process in which essentially completely desalinated water is produced from a saline source in a single pass through a semipermeable membrane. The term pressure osmosis is used here to describe similar processes in which only partial salt removal is achieved, or in which the permeate is actually enriched in salt relative to the pressurized solution. Thermodynamic pressure requirements for various degrees of separation are calculated.

Membrane materials capable of yielding an enriched permeate have not been developed to date. Two model membranes suitable for the purpose are suggested, and their expected performance is calculated.

The last few years have seen a rapidly increasing interest in the use of reverse osmosis for water desalination (1, 2). In reverse osmosis, saline water under a suitably high pressure is placed in contact with a membrane which is permeable to water but relatively impermeable to salt. Desalinated water is collected on the other side of the membrane at lower pressure (usually atmospheric), and concentrated brine is formed on the high pressure side and discarded.

Present emphasis is on the use of membranes sufficiently permeable to water and sufficiently impermeable to salt to make possible the production of potable water in a single step of this kind. It is clear, however, that multiple pass processes can also be used in which a smaller degree of salt removal is obtained in each step. Furthermore, it is possible in principle to perform a rather similar operation, in which the solution forced through the membrane has a higher salt content than the feed solution and the desired product water is retained on the high pressure side of the membrane.

PRESSURE REQUIREMENTS

If two chambers designated ' and ", at different pressures p' and p'' , are separated by a membrane, flow will occur under isothermal conditions only in such a manner that the entropy production in the system, dS_i , is positive. Thus, we require that

$$-T dS_i = \Delta\mu_w dn'_w + \Delta\mu_s dn'_s < 0 \quad (1)$$

where n_w and n_s are moles of water and salt, respectively, T is temperature, and

$\Delta\mu_w = \mu'_w - \mu''_w$ and $\Delta\mu_s = \mu'_s - \mu''_s$ are chemical potential differences for water and salt across the membrane.

If the membrane is permeable to water only, then the requirement becomes

$$\Delta\mu_w dn'_w = \bar{v}_w(\Delta p - \Delta\pi)dn'_w < 0 \quad (2)$$

where $\Delta p = p' - p''$, \bar{v}_w is the partial molar volume of water and has been assumed to be pressure- and concentration-independent, and $\Delta\pi = \pi' - \pi''$ is the difference between the osmotic pressures of the two solutions. Thus, flow will occur from chamber ' to chamber '' (i.e., $dn'_w < 0$) for $\Delta p > \Delta\pi$. The transfer of pure water from a 0.6 molal (*m*) sodium chloride solution (near sea water concentration) into pure water (or a very dilute salt solution) thus requires a minimum pressure of 26 atm (3). The volume of the high pressure solution decreases by $\sim 18 \text{ cm}^3$ for each mole of desalinated water recovered.

If the membrane is permeable to salt and not to water, then the requirement becomes

$$\Delta\mu_s dn'_s = (RT \ln \frac{a'_s}{a''_s} + \bar{v}_s \Delta p) dn'_s < 0 \quad (3)$$

where a'_s and a''_s are the salt activities of the two solutions measured at the same pressure, and \bar{v}_s is the partial molar volume of salt and has been assumed to be independent of pressure and salt concentration. Thus, for dn'_s negative we require

$$\Delta p > \frac{RT}{\bar{v}_s} \ln \frac{a'_s}{a''_s} \quad (4)$$

The removal of salt from a less concentrated sodium chloride solution into a 0.6*m* solution thus requires a pressure which increases as the salt concentration decreases, reaching about 1.1×10^4 atm at 0.006 *m*, based on 25°C sodium chloride activities given by Robinson and Stokes (4) and a partial molar volume, \bar{v}_s , of $18 \text{ cm}^3/\text{mole}$. Practically speaking, this is probably an uninterestingly high pressure, even though the volume decrease of the high pressure solution is small, being only 0.2 cm^3 per mole of desalinated water produced from a 0.6*m* solution, and even though most of the salt would be removed (in a reversible system) at substantially lower pressures.

The two possibilities we have thus far considered are unachievable special cases of the general problem. All real membranes have some permeability to both salt and water, and hence neither dn'_w nor dn'_s is, strictly speaking, zero in any real case. Under these circumstances the condition for the occurrence of a spontaneous process becomes

$$\Delta\mu_w dn'_w + \Delta\mu_s dn'_s = (\bar{v}_w dn'_w + \bar{v}_s dn'_s) \Delta p - \bar{v}_w \Delta\pi dn'_w + RT \left(\ln \frac{a'_s}{a''_s} \right) dn'_s < 0 \quad (5)$$

or

$$(\bar{v}_w dn'_w + \bar{v}_s dn'_s) \Delta p < \bar{v}_w \Delta\pi dn'_w - RT \left(\ln \frac{a'_s}{a''_s} \right) dn'_s \quad (6)$$

In principle, many different transport possibilities exist. We have already considered, for example, a case in which a moderately concentrated brine is in contact with the low pressure side of the membrane and pure salt passes from a dilute salt solution through the membrane and into the brine.

In practice, a situation of this kind cannot be readily achieved. Since a substantial pressure difference is to be maintained across the membrane, it must be supported on a finely porous substrate, and providing effective circulation within that substrate on the low pressure side will generally not be practical. Instead, the low pressure solution in immediate contact with the membrane will tend to have a composition equal to the composition of the transported material, and circulating a different solution past that side of the membrane but at some distance from it will be to no avail. Most commonly, then, in a practical pressure osmosis device the low pressure channel will have only an outlet, and the solution within it will be just what comes through the membrane.

On the high pressure side, of course, no supporting structure is required. Here, with suitable provisions for mixing, it should be possible to maintain surface concentrations very near bulk concentrations, so long as membrane fluxes are not excessive.

A particularly useful set of boundary conditions is thus

$$c' = c'_b \quad (7)$$

and

$$c'' = 55.5 \frac{dn'_s}{dn'_w} \quad (8)$$

where the c 's are molal concentrations, c'_b is the bulk concentration of the feed solution, and the factor 55.5 is necessary to convert the mole ratio into molal concentration units. Substituting from Eq. (8) into Eq. (6), we obtain

$$\Delta p > \frac{55.5\bar{v}_w \Delta\pi - RTc'' \ln a'_s/a''_s}{55.5\bar{v}_w + c''\bar{v}_s} \quad (9)$$

as the condition for flow from the high to the low pressure chamber ($dn'_w < 0, dn'_s < 0$).

Robinson and Stokes (4) have critically evaluated and tabulated the thermodynamic properties of sodium chloride solutions at 25°C. We have used their data to construct the curves of Figure 1, where the minimum pressure of Eq. (9) is plotted as a function of permeate concentration, for various feed concentrations. The curves all show a zero pressure requirement when permeate and feed concentrations are equal, as must be the case. Finite pressure requirements on either side of this minimum are an equally obvious thermodynamic result, since a zero requirement or a requirement of opposite sign would imply spontaneous unmixing of a sodium chloride solution of initially uniform composition.

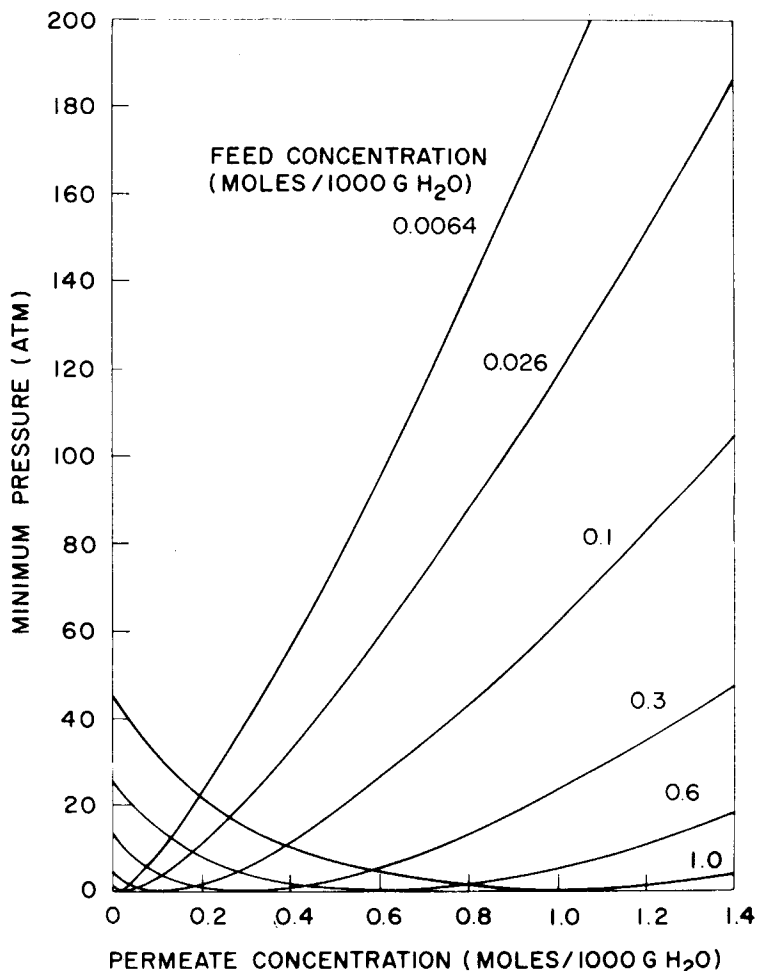


Fig. 1. Minimum pressure requirements. Each curve indicates the minimum pressure thermodynamically required at 25°C to produce permeates of various salt contents from a feed solution of the indicated sodium chloride content. Concentrations are in molal units, i.e., moles NaCl/1000 g H₂O.

The curve marked 0.0064*m* feed concentration is of special interest, since it gives a measure of the minimum pressure required to force more concentrated sodium chloride solutions out of a fully desalinated (accepting 250 ppm Cl⁻ or 0.007*m* as a standard of potability) feed water. Such a situation would prevail in the last part of a system designed to produce potable water from a saline feed water by forcing a concentrate through a suitable membrane under pressure. The curve marked 0.6*m* is also of special interest, since it provides a reasonably accurate measure of the minimum pressures required to force solutions of various salt concentrations out of sea water of normal salinity.

MEMBRANE MATERIALS

The curves of Fig. 1 state only what is thermodynamically necessary; they give

no measure of what is practically possible. A given c'' to c' relationship can be obtained only if a membrane of suitable properties can be found.

The literature on membranes more permeable to water than to salt is already rather extensive. Desalination has been accomplished using cellulose acetate (1, 5) and ion-exchange membranes, (6) and many other materials have been shown to have some potential for this purpose. Flow-coupling has been shown to be of minor importance in the cellulose acetate membranes, (2, 7) but can be expected to be quite important in the usual ion-exchange membranes and other materials less selective against salt transport.

No similarly extensive study of membranes for the inverse process has been reported, although Kraus, Marcinkowsky, Johnson and Shor (8) recently observed small degrees of salt enrichment on forcing aqueous MgCl_2 and CaCl_2 solutions through porous Vycor glass. In the absence of more extensive experimental data, it is of some interest to speculate on where such membranes may be found.

It is most important to recognize that strong coupling between salt and water flows will be essential in any successful salt permeable membrane. By expressing the flow of salt through the membrane, F_s , as

$$F_s = -L_{sw}\Delta\mu_w - L_{ss}\Delta\mu_s \quad (10)$$

where L_{sw} and L_{ss} are appropriate phenomenological coefficients, we can use the arguments already stated in discussing membranes permeable to salt only in order to show that at significant salt concentration differences across the membrane, uninterestingly large pressures are required to reverse the sign of $\Delta\mu_s$. Thus, $\Delta\mu_s$ will generally cause salt flow into the low concentration chamber, and flow of salt in the desired direction will occur only if the coupling coefficient L_{sw} is sufficiently large so that the term $L_{sw}\Delta\mu_w$ outweighs the term $L_{ss}\Delta\mu_s$.

NEUTRAL MEMBRANES

The desired degree of coupling could presumably result from any number of phenomena, but the most obvious model is that of a membrane having pores which contain both salt and water, with this mixture passing through the pores by viscous flow. Such a membrane will provide coupled salt and water flow in any case and, in particular, can deliver to the low pressure side a permeate which is higher in salt concentration than the feed solution, provided that the pore liquid itself has a higher salt content than the feed solution.

If we characterize the equilibrium salt sorption properties of such a membrane by a distribution coefficient, K , expressed as the molar salt concentration of the solution within the pores divided by the molar salt concentration of the external solution, then it is reasonable to expect that this equilibrium distribution coefficient will be obeyed at both membrane-solution interfaces under conditions of a finite flow rate through the membrane. (We assume that the boundary layers are dispersed by suitable stirring.) The form of the flow rate-permeate concentration relationship

to be expected in such a porous membrane has been discussed elsewhere (9) for the case of water permeable membranes, and the results are directly applicable to neutral salt-permeable membranes. We find that

$$C'' = \frac{K' C' \exp \left(-\frac{ut\lambda}{D} \right)}{K'' - 1 + \exp \left(-\frac{ut\lambda}{D} \right)} \quad (11)$$

where C' and C'' are the molar salt concentrations in the external solution at the high and low pressure interfaces, respectively, K' and K'' are the distribution coefficients across those interfaces as defined above, u is the fluid velocity in the pore with flows from the high pressure to the low pressure chamber having a negative sign, λ is the membrane thickness, t is a pore tortuosity factor, and D is the diffusion coefficient for salt in the pore fluid. Thus, at low flow rates and with thin membranes no separation is accomplished; but at high flow rates (in the negative y direction) through sufficiently thick membranes, a salt concentration ratio $C''/C' = K'$ is approached.

It is thus necessary to find membranes having a suitably high value of K , and yet having sufficiently open porosity so that the pore walls do not interfere with the transport of salt by water passing through the pores. Vieth (10) has reported that cellulose nitrate membranes deliberately made porous by the addition of rather large amounts (25%–40%) of TeBr_4 exhibit distribution coefficients greater than unity in our present terms. However, no evidence of preferential permeability to salt was found in these membranes, and this has been attributed to immobilization of part of the salt in the cellulose nitrate portion of the membrane. In our picture, this behavior can be attributed to frictional interactions between the solute and the membrane material which substantially decouple the salt and water flows.

A similar membrane could be based on the so-called snake-cage ion-retardation resins. Distribution coefficients for NaCl between beads of one resin of this kind and an external solution have been measured by Hatch, Dillon, and Smith (11) and their results are reproduced in Fig. 2. Even at an external concentration close to $0.5m$, a distribution coefficient greater than 1.5 is observed, indicating that significant desalination of solutions of sea water concentration might be possible.

To our knowledge, no snake-cage membrane has yet been made and tested. Therefore, it is not known whether adequate coupling of water and salt flows would occur to make such membranes successful. Let us suppose for the moment, however, that the kinetic salt-pore-wall interactions are small. The distribution coefficient data of Fig. 2 can be adequately represented by the equation

$$K' = \frac{1}{c' + 0.18} \quad (12)$$

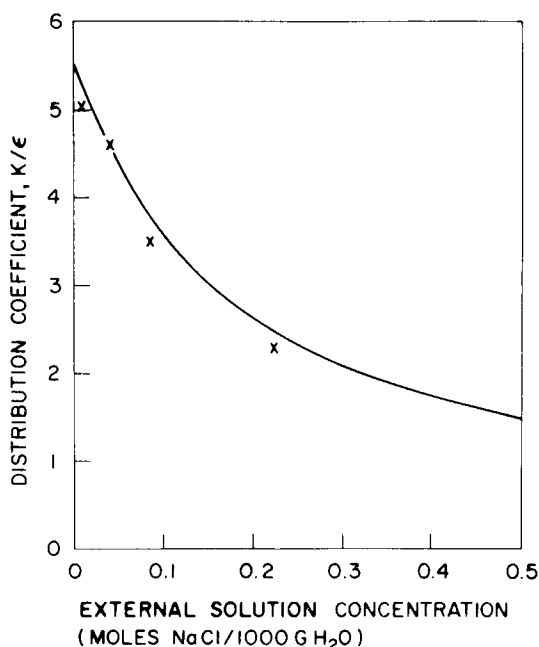


Fig. 2. Sodium chloride distribution coefficients for a snake-cage resin. Data of Hatch, Dillon, and Smith (11). Distribution coefficient is expressed as salt concentration in water within resin divided by salt concentration in external solution.

The solid line in Fig. 2 represents this equation.

If feed water of initial concentration c'_0 is progressively desalinated by having a portion of it passed through the membrane, solute conservation requires that the feed water concentration, c' , be related to the concentration of the permeate, c'' , by the expression

$$d(c'\phi) = c'd\phi + \phi dc' = c''d\phi \quad (13)$$

where ϕ is the fraction of the initial water remaining on the feed water side of the membrane. According to Eq. (11), at sufficiently high flow rates $c'' = K'c'$ (if we neglect the small numerical difference between molar and molal concentration units). So from Eq. (12),

$$c'' = \frac{c'}{c' + 0.18} \quad (14)$$

and if Eq. (13) is integrated with the boundary condition $c' = c'_0$ for $\phi = 1$,

$$\phi = \left(\frac{c'}{c'_0} \right)^{0.22} \left(\frac{0.82 - c'_0}{0.82 - c'} \right)^{1.22} \quad (15)$$

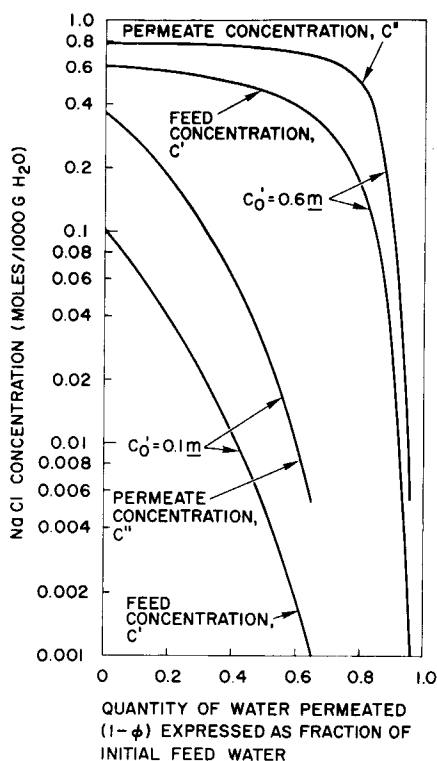


Fig. 3. Hypothetical desalination curve for a snake-cage resin membrane. The initial feed solution concentration is assumed to be $0.6m$ NaCl in the upper curves and $0.1m$ NaCl in the lower curves. The curves indicate permeate and feed solution salt concentrations as a function of the fraction of the feed water permeated through the membrane.

In Fig. 3 we show c' and c'' as a function of ϕ for $c'_0 = 0.6m$, and a hypothetical membrane having the sorption properties of the snake-cage resin of Hatch, Dillon, and Smith (11).

It is immediately clear that sea water desalination with a membrane of this kind will require a multistage process if reasonable water recoveries are to be achieved. The salt concentration in the feed compartment reaches $0.007m$ only after the volume has been reduced to 7% of the original feed volume. If the permeate is collected in successive batches, an additional 19% of the original volume is collected as a permeate with a concentration of less than $0.6m$, but several stages of treatment would be required, for example, to reduce half the feed water to a concentration of $0.007m$ and increase the concentration of the remainder to $1.2m$.

Fig. 3 can be used to obtain results for lower values of c'_0 by simply expanding the appropriate portion of the upper curve to fill the entire ϕ scale. This has been done in the lower curves for $c'_0 = 0.1m$. Under these conditions, 49% of the feed

water remains in the high pressure chamber when the concentration there reaches $0.007m$, thus being deasinated in a single stage; and the first permeate is already at a concentration 3.5 times the feed concentration and might well be discarded without further treatment. A substantial amount of the permeate, approximately 19% of the initial feed water, can be collected at concentrations of less than $c'_0 = 0.1m$ before the feed water reaches $0.007m$, and this amount, at least, would be recycled.

MOSAIC MEMBRANES

A second membrane potentially useful in this application is the ion-exchange mosaic. Ion-exchange membranes have been considered for use as water permeable pressure osmosis membranes because exclusion of coions reduces coion flux through the pores, and the condition of electro-neutrality requires that counterion flux be limited as well. A mosaic membrane would consist of roughly equal quantities of suitably subdivided anion and cation exchange material intimately mixed together. Water flowing through the pores of each material would carry along large numbers of counterions which are, in general, enriched relative to their concentrations in the external solution, and charge neutrality would be satisfied because the ions of opposite sign could come together at the outlets of the anion and cation pores.

Membrane inhomogeneities were invoked by Sollner (12) in an early explanation of anomalous osmosis. In later papers he suggested (13) that a mosaic structure of the kind proposed here might be important in natural membranes and constructed model systems (14, 15) to demonstrate the existence of circulating currents within such membranes. More recently, de Kőrösy and Shorr (16) succeeded in preparing a membrane with adjacent anion and cation regions, and de Kőrösy (17) examined its behavior in salt diffusion experiments. Kedem and Katchalsky (18) have presented a much more extensive mathematical treatment of such membranes than we will attempt here. The present treatment is very similar to theirs, but is better adapted to the case where large concentration differences exist across the membrane.

As in the case of the electrically neutral membranes, mosaic membranes will be effective only if flow through the pores is essentially viscous in nature and kinetic ion-pore-wall interactions are small. It is perhaps more likely that a practical membrane of this type can be perfected than one of the electrically neutral type, since with mosaic membranes salt inclusion is due to coulomb forces, and significant degrees of counterion inclusion can be achieved with wide pore diameters.

A mosaic membrane of this kind should be describable in much the same terms as are used to describe normal ion-exchange membranes. The Meyer-Sievers model of charged membranes as extended in recent years by Schmid (19), Lauger and Kuhn (20), and Schlögl (21) should be particularly useful, since these authors assume viscous flow conditions in the pores, and this is the situation of real interest. The model further assumes a fixed charge density low enough (and a pore diameter small enough) so that the membrane can be considered an essentially homogeneous

mixture of fixed and mobile charges. This last limitation is avoided in the more detailed models of Dresner (22) and Lauger (23), but we will restrict our analysis to the simple case.

We will assume that our mosaic membrane consists of a closely packed array of cylinders of ion-exchange materials, each having a length, λ , equal to the membrane thickness. We will discuss only its behavior with respect to a solution of a single uni-univalent electrolyte. The flux of negative ions within the pores of the anion-exchange cyclinders containing a fixed charge of density X_+ moles/cm³ of pore volume will be*

$$F_{-+} = -\frac{D_{-+}C_{-+}}{RT} \frac{d\mu_{-+}}{dy} + C_{-+}u_+ \quad (16)$$

where D_{-+} , μ_{-+} , and C_{-+} are the diffusion coefficient, chemical potential, and molar concentration of the negative ions within the pores of the positively charged exchanger, and u_+ is the linear fluid flow velocity within these pores. The flow of singly charged positive ions in the pores of this same material is

$$F_{++} = -\frac{D_{++}C_{++}}{RT} \frac{d\mu_{++}}{dy} + C_{++}u_+ \quad (17)$$

where D_{++} , μ_{++} , and C_{++} are the diffusion coefficient, chemical potential, and concentration of the positive ions within the pores of the positively charged exchanger. The flows F_{--} and F_{+-} of negative and positive ions, respectively, in the pores of the cation exchanger (with charge density X_- moles/cm³ pore volume) are given by similar equations, with the last (or only) subscript changed to indicate that the quantity is evaluated within the pores of the negatively charged material, i.e.,

$$F_{--} = -\frac{D_{--}C_{--}}{RT} \frac{d\mu_{--}}{dy} + C_{--}u_- \quad (18)$$

and

$$F_{+-} = -\frac{D_{+-}C_{+-}}{RT} \frac{d\mu_{+-}}{dy} + C_{+-}u_- \quad (19)$$

Even with the substantial simplifications already made, the general solution of the equations is unwieldy, and we will examine here only the limiting case where the exclusion of coions from the pores is sufficiently good to permit the approximation that the concentrations C_{++} and C_{--} and the related flows F_{++} and F_{--}

* A rigorous justification of Eqs. (16)–(19) requires a careful definition of the diffusion coefficient, an accounting for the changes in solution density which accompany concentration changes, and so on. In the dilute solutions of interest here, we can accept the D 's simply as Fick's law diffusion coefficients and the u 's as volumetric flow rates per unit cross-sectional pore area.

are all zero. Then charge neutrality requires that $C_{-+} = X_+$ and $C_{+-} = X_-$, and if there is no external current flow, that $F_{-+} = F_{+-}$. Thus, Eq. (16) becomes

$$F_{-+} = -\frac{D_{-+}X_+}{RT} \frac{d\mu_{-+}}{dy} + X_+u_+ \quad (20)$$

Since at steady state F_{-+} and u_+ are constants, under these conditions

$$\frac{\Delta\mu_{-+}}{t\lambda} = -\frac{RT}{D_{-+}X_+} F_{-+} + \frac{RT}{D_{-+}} u_+ \quad (21)$$

where $t\lambda$ is the length of the pores.

We have already remarked that the effluent concentration generally determines the concentration of the solution in contact with the membrane on the effluent side; hence, the salt concentration on the effluent side of the membrane, C'' , is given by

$$C'' = \frac{\varepsilon_+ F_{-+}}{\varepsilon_+ u_+ + \varepsilon_- u_-} \quad (22)$$

where ε_+ and ε_- are the fractional cross-sectional areas of the membrane occupied by pores in the positively and negatively charged ion-exchange cylinders, respectively. Further, if the external solutions obey Henry's law, then

$$\Delta\mu_{-+} = RT \ln \frac{C'}{C''} - \mathcal{F} \Delta\psi \quad (23)$$

and inserting Eqs. (22) and (23) into Eq. (21) yields

$$\frac{RT}{t\lambda} \ln \frac{C'}{C''} - \frac{\mathcal{F} \Delta\psi}{t\lambda} = -\frac{RTC''}{D_{-+}X_+} \frac{\varepsilon_+ u_+ + \varepsilon_- u_-}{\varepsilon_+} + \frac{RTu_+}{D_{-+}} \quad (24)$$

A similar expression may be derived from Eq. (19) to yield

$$\frac{RT}{t\lambda} \ln \frac{C'}{C''} + \frac{\mathcal{F} \Delta\psi}{t\lambda} = -\frac{RTC''}{D_{+-}X_-} \frac{\varepsilon_+ u_+ + \varepsilon_- u_-}{\varepsilon_-} + \frac{RTu_-}{D_{+-}} \quad (25)$$

and if $\Delta\psi$ is eliminated, the result is

$$C'' = \frac{\varepsilon_- \varepsilon_+ X_- X_+ \left(D_{-+} u_- + D_{+-} u_+ - \frac{2D_{+-} D_{-+}}{t\lambda} \ln \frac{C'}{C''} \right)}{(\varepsilon_+ u_+ + \varepsilon_- u_-)(D_{+-} X_- \varepsilon_- + D_{-+} X_+ \varepsilon_+)} \quad (26)$$

A mosaic membrane will work most effectively for our purpose if the external solution resistance between positive and negative regions is negligible. This has been assumed above by assuming uniform concentrations on both sides of the membrane and assuming $\Delta\psi$ to be the same for the positively and negatively charged cylinders. The latter restriction is relatively easily removed if simplifying assumptions are made, and it can be shown, as one might expect, that a suitable criterion for negligible difference in the $\Delta\psi$'s is that the external solution resistance between the ends of adjacent cylinders be small compared with the electrical resistance along the length of a cylinder.

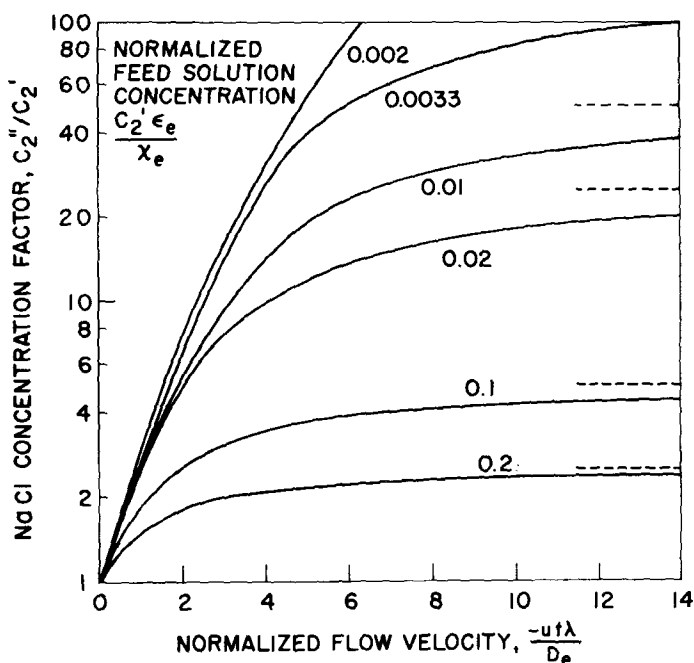


Fig. 4. Salt concentration factors for a hypothetical mosaic membrane. The ratio of the permeate concentration (C'') to the feed concentration (C') is shown as a function of linear flow velocity ($-u$) through the membrane pores, normalized for pore length ($t\lambda$) and the diffusion coefficient (D) for salt in the pore liquid. Feed solution concentrations are normalized for fixed charge density in the membrane, assumed here to be the same in the cationic and anionic portions. The dashed lines are high velocity asymptotes for the lower curves.

The result given in Eq. (26) is illustrated in Fig. 4 for the case of a uni-univalent salt whose anion and cation have equal mobility, and a membrane with equivalent positively and negatively charged cylinders; i.e., $\varepsilon_- = \varepsilon_+ = \varepsilon$, $X_- = X_+ = X$, $D_{-+} = D_{+-} = D$, and $u_+ = u_- = u$. In this case,

$$C'' = \frac{X}{2} \left(1 - \frac{D}{ut\lambda} \ln \frac{C'}{C''} \right) \quad (27)$$

In using Fig. 4 we might choose a fixed charge density of 3 meq/cm³ of pore volume as being near the achievable upper limit in a viscous flow (i.e., highly porous) membrane. It is clear that for a 0.6*m* solution ($C'/X = 0.2$ and near sea water concentration), velocities giving $-ut\lambda/D > 3$ will afford a reject brine enriched in salt by a factor of 2, and that brine of sea water concentration can be forced from a 0.006*m* solution ($C'/X = 0.002$ and near potable concentration) at $-ut\lambda/D > 6$. Since we have assumed negligible kinetic interaction between pore wall and solute,

it is reasonable to assume that $D \approx 1 \times 10^{-5}$ cm²/sec, and if we assume that $t\lambda = 100$ microns, then the requirement ($-\mu t\lambda/D > 6$) becomes $-u > 6 \times 10^{-3}$ cm/sec. If 50% total membrane porosity is assumed, total flow will be 3×10^{-3} cm³/cm²-sec. The fact that boundary layer considerations make the use of substantially higher flow rates in combination with smaller pore lengths, as is permitted by Eq. (26), undesirable has been discussed elsewhere for a similar case (9).

The pressure required to reach any desired value of $-ut\lambda$ depends upon the pore size of the membrane. Given a membrane with equivalent hydraulic pore radius r , the flow rate will be (9)

$$ut\lambda = -\frac{r^2}{8\eta}(\Delta p - \Delta\pi' + \Delta\pi'') \quad (28)$$

where $\Delta\pi'$ ($\Delta\pi''$) is the osmotic pressure of the ' (") solution minus the osmotic pressure of the pore fluid within the pore at the interface with the ' (") solution.

If a mosaic membrane were operated at a sufficiently high flow rate, the limiting permeate concentration would be $c'' = X/2$ (again neglecting the small numerical difference between molar and molal concentration units) for all feed concentrations. Thus, Eq. (13) becomes

$$\frac{dc'}{\frac{X}{2} - c'} = \frac{d\phi}{\phi} \quad (29)$$

or, if we integrate with the boundary conditions $c' = c'_0$ for $\phi = 1$,

$$\phi = \frac{X - 2c'_0}{X - 2c'} \quad (30)$$

This equation can be used like Eq. (14) to evaluate the high-flow-rate limiting case. For $X = 3.0$ meq/cm³ of pore fluid, a 0.6*m* feed can be desalinated to $c' = 0$ by removing 40% of the water (i.e., $\phi = 0.60$). (According to Eq. (30), further water removal will reduce c' to negative values, an anomaly which arises because the assumption that c'' can be kept equal to X at sufficiently high $-u$'s fails as c' approaches zero.) With a less saline feed, say 0.10*m*, but otherwise the same assumptions, $c' = 0$ at $\phi = 0.93$.

These calculations for mosaic membranes involve three major assumptions, all of which may be approached, but not completely satisfied, in practice. They are (1) that $-\mu t\lambda/D$ is sufficiently high to approach maximum concentration factors; (2) that coions are completely excluded from the pores; and (3) that flow within the pores is viscous, i.e., that there is no kinetic interaction between the counterions and the pore walls.

We have already seen that assumption (1) can be closely satisfied by arbitrarily making $t\lambda$ sufficiently large, at the expense of membrane permeability. Assumption (2) is not easily satisfied at high external salt concentrations, but deviations are

actually favorable to our case provided that they do not affect assumption (3). Failure to exclude all coions increases the counterion concentration as well, and the result is a more concentrated permeate. Assumption (3) is undoubtedly the most troublesome. It is well known (24) that counterion mobilities in ion-exchange resins are generally lower than the free solution values, a result which could be of critical importance here. On the other hand, the very high transference numbers for water observed, for example, by Lakshminarayanaiah and Subrahmanyam (25) in electro-osmotic measurements suggest that achieving the required degree of coupling between counterion and water transport is by no means out of the question.

ACKNOWLEDGEMENT

The author would like to thank Dr. H. K. Lonsdale and Prof. O. Kedem for suggesting significant revisions in the manuscript. This research was supported by the Office of Saline Water, U. S. Department of the Interior, under Contract 14-01-0001-250.

REFERENCES

1. S. LOEB AND F. MILSTEIN, *Dechema Monograph.*, **47** (1962) 707.
2. U. MERTEN, *Proceedings First International Symposium on Water Desalination*, Washington, D. C., October 3-9 (1965), paper SWD/44, in press.
3. R. W. STOUGHTON AND M. H. LIETZKE, *J. Chem. Eng. Data*, **10** (1965) 254.
4. R. A. ROBINSON AND R. H. STOKES, *Electrolyte Solutions*, Butterworths Sci. Publ., London (1959) pp. 476, 481.
5. C. E. REID AND E. J. BRETON, *J. Appl. Polymer Sci.*, **1** (1959) 133.
6. J. G. MCKELVEY, JR., K. S. SPIEGLER AND M. R. J. WYLIE, *Chem. Eng. Progr. Symp. Ser.* **55**, No. 24 (1959) 199.
7. H. K. LONSDALE, U. MERTEN AND R. L. RILEY, *J. Appl. Polymer Sci.*, **9** (1965) 1341.
8. K. A. KRAUS, A. E. MARCINKOWSKY, J. S. JOHNSON AND A. J. SHOR, *Science*, **151** (1966) 194.
9. U. MERTEN, *Desalination by Reverse Osmosis*, Massachusetts Institute of Technology Press, to be published.
10. W. VIETH, Department of Chemical Engineering, Massachusetts Institute of Technology, private communication.
11. M. J. HATCH, J. A. DILLON AND H. B. SMITH, *Ind. Eng. Chem.*, **49** (1957) 1812.
12. K. SOLLNER, *Z. Elektrochem.*, **36** (1930) 36, 234.
13. K. SOLLNER, *Biochem. Z.*, **244** (1932) 370.
14. R. NEIHOF AND K. SOLLNER, *J. Phys. Chem.*, **54** (1950) 157.
15. R. NEIHOF AND K. SOLLNER, *J. Gen. Physiol.*, **38** (1955) 613.
16. F. DE KÖRÖSY AND J. SHORR, *Nature*, **197** (1963) 685.
17. F. DE KÖRÖSY, *Nature*, **197** (1963) 685.
18. O. KEDDEM AND A. KATCHALSKY, *Trans. Faraday Soc.*, **59** (1963) 1918.
19. G. SCHMID, *Z. Elektrochem.*, **56** (1952) 181.
20. P. LAÜGER AND W. KUHN, *Ber. Bunsenges. Physik. Chem.*, **68** (1964) 4.
21. R. SCHLÖGL, *Z. Physik. Chem.*, NF **3** (1955) 73.
22. L. DRESNER, *J. Phys. Chem.*, **67** (1963) 1635.
23. P. LAÜGER, *Ber. Bunsenges. Physik. Chem.*, **68** (1964) 352.
24. F. HELFFERICH, *Ion Exchange*, McGraw-Hill Book Company, New York (1962) p. 308.
25. N. LAKSHMINARAYANAIAH AND V. SUBRAHMANYAN, *J. Polymer Sci.*, **A2** (1964) 4491.