JOURNAL OF APPLIED POLYMER SCIENCE VOL. 16, PP. 771–782 (1972)

The Role of Membrane Pressure in Reverse Osmosis

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Synopsis

Liquid transport occurs through reverse osmosis membranes as a result of an applied pressure differential. The pressure within the membrane continuum is an important thermodynamic parameter in the formulation of solution-diffusion models for this process. It is shown that this membrane pressure is the same throughout the membrane for supported flat and tubular membranes and for hollow fibers. The use of this parameter in calculating the induced concentration differential is discussed.

INTRODUCTION

In recent years, reverse osmosis has emerged as an attractive process for removing solutes from liquids to produce potable water and for pollution abatement, to mention but a few applications. Membranes in the form of flat sheets or tubular geometries have been used. The advent of hollow fibers for this purpose has opened up new horizons for commercial application of this method. Regardless of geometry, the external driving force for the transport of liquid through the membrane is the application of pressure to the feed solution so that a pressure differential exists across the membrane. It is a question of mechanisms as to how this phenomenologic driving force operates within the membrane to effect liquid transport. According to the solution-diffusion models, the pressure differential induces a concentration gradient of liquid within the membrane, and transport proceeds by simple Fickean diffusion.[1] It is the purpose of this paper to explore further the details associated with transport of the liquid species by this mechanism for the above-mentioned membrane geometries used in reverse osmosis. Special attention is paid to the pressure within the membrane, since this is believed to be a key parameter to a correct formulation of a solution-diffusion model. Its role in flat membranes has been considered previously,[2,3] and an extension to include hollow fibers is made here.

In most solution-diffusion analyses of reverse osmosis, the concentration gradient is considered to arise by the Poynting effect, in that the applied pressure increases the liquid activity within the membrane at the upstream surface and thereby increases the swelling there beyond the normal solubility of the liquid in the polymer. This is a misapplication of this concept, and a correct formulation reveals that no increase in swelling should occur at the upstream surface of a flat membrane but that there will be a

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decrease in swelling at the downstream surface instead.[2] A direct experimental proof of this point has been made.[3] It is true that the *chemical potential* of the liquid within the membrane at the upstream surface will be increased by the application of pressure, and the activity there may be raised depending on the definition employed for the latter. A more useful definition is to write the chemical potential for the solvent (species 1) as

$$\mu_1 = \mu_1^0 + RT \ln a_1 + V_1 (p - p_r) \tag{1}$$

where now the activity of the solvent, a_1, is primarily dependent on composition and will have only a secondary dependence on pressure caused by volume changes on mixing and alteration in intermolecular interaction by increased pressure. At equilibrium, the chemical potential of species 1 must be the same in both phases, and consequently from eq. (1) the activity of species 1 as defined there will be the same in each phase unless the pressures in the two phases are different so long as the partial molal volumes of species 1 are the same in both phases. Thus, barring the secondary effects, we would predict that the degree of swelling of a polymer immersed in a solvent (which does not completely dissolve it) will be independent of the pressure applied to the solvent if the pressure within the polymer is the same as the liquid pressure. If the pressures in the two phases can be made different somehow, then the activity of solvent in the polymer or membrane phase, a_1^m, will be related to the activity in the liquid phase, a_1^s, by

$$a_1^m = a_1^s e^{V_1(p - p_m)/RT} \tag{2}$$

where p and p_m are the pressures in the liquid and membrane phases, respectively. Thus, in this case, the degree of swelling of the polymer will change as a primary consequence of the pressure difference. For $p > p_m$, the degree of swelling will increase, and for $p < p_m$, it will decrease. Equation (2) may be considered as a correct statement of the Poynting effect.[4] Since equilibrium will prevail at both membrane surfaces, this condition must be applied at each surface. It is thus clear that the membrane pressure is a necessary consideration.

In the case of a soft polymer simply immersed in a liquid, it is easily visualized that the pressure is always the same in both phases. Ham et al.[5] have investigated the effect of pressure on vulcanized rubbers immersed in highly swelling solvents. They found that the degree of swelling changed by no more than about 3% when the pressure applied to the solvent was 30,000 psi. This change was found to be a decrease or increase, depending on the polymer or solvent employed. Thus, all effects are clearly of the secondary type described above and can be totally ignored at the modest pressures employed in reverse osmosis.

To pursue the application of eq. (2) in reverse osmosis, it is necessary to know the membrane pressure for a given membrane geometry. The concept of pressure within a material with elastic characteristics raises some profound questions. If this material is composed of a component which has load bearing characteristics (the polymer) and one that does not (dis-

solved solutes such as the solvent), is the pressure at a point the same for all of the components? Pressure is a macroscopic, not a molecular concept, and since macroscopically the membrane plus dissolved solvent is a homogeneous, single phase, we are compelled to consider the pressure to act on the continuum. When forces are applied to an elastic material, the normal stresses that result may not be isotropic. As a result of this, a rational definition of pressure is taken to be the average of the principle normal stresses,[6] that is, the membrane pressure will be

$$p_m = -{}^1/_3 \text{ trace } (\sigma) \tag{3}$$

where σ is the complete stress tensor. The stress tensor may be computed in principle from the equations of elasticity solved with the applicable boundary conditions. We identify the pressure computed from eq. (3) with the thermodynamic pressure required in eq. (1). The general applicability of this identification has apparently never been explored. Exceptions may be envisioned, e.g., systems which do not readily attain local thermodynamic equilibrium or in cases where Poisson's ratio is much less than 0.5. We postulate that it should be applicable to membranes which are appreciably swollen by the solvent employed, since this would facilitate the attainment of the above conditions.

Individual components of σ generally vary with position within the material. Interestingly however, we will show next that, for the important cases of flat and tubular membranes and hollow fibers, p_m is a constant throughout the membrane.

SUPPORTED MEMBRANES

For reverse osmosis usage, flat membranes are generally supported on the downstream side by a porous plate, as shown in Figure 1 where a totally dense membrane is pictured. Asymmetric membranes such as the Loeb type, which have a porous matrix overlaid by a totally dense skin, are analogous to the situation in Figure 1 for our purposes, as we can consider the porous matrix of the membrane as a simple extension of the porous plate. We will consider that the pores in the support plate are vanishingly small so that there is no appreciable stress concentration within the membrane

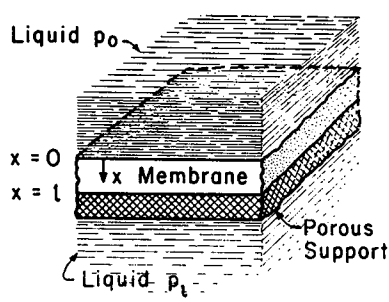

Fig. 1. Flat, supported membrane.

in the vicinity of a pore; however, as a practical matter, the pores should be large enough to easily transmit the permeate. Further, we will assume that the deswelling which has been shown to occur at the downstream membrane surface[2] is small enough so that appreciable lateral forces do not develop. For such conditions, it was demonstrated earlier using a swollen polymer network as the membrane[2] that it is necessary to equate the membrane pressure p_m to the upstream feed pressure p_0 to properly describe the induced concentration gradient and the resulting flux. Mechanically, this assertion can be understood by realizing that the force the upstream fluid pressure p_0 exerts downward on the membrane is transmitted through the membrane to the support plate, which in turn exerts an equal force upward. The pressure on the membrane continuum is therefore p_0 throughout.

It may be helpful as an analogy to view the membrane as a liquid with a very high surface tension which does not wet the porous support plate (and therefore does not enter the pores until very high pressures are applied). This fluid "membrane" maintains its identity when a feed liquid is placed above it so long as the "membrane fluid" is not miscible in the feed liquid. Miscibility of the feed in the "membrane" is permissible. When a pressure p_0 is applied to the feed liquid, it is eminently clear that the pressure in the "membrane" is also p_0. Now, bestowing load-bearing characteristics, i.e. elasticity, to the membrane per se does not destroy this analogy. Thus, barring extraordinary conditions, it should be clear that p_m in a flat membrane is p_0. This is also true for supported tubular membranes whose thicknesses are very small compared to their diameters, provided the membrane and support tubes are properly sized so that stretching or compression does not occur when pressurized.

Application of eq. (2) to the membrane in Figure 1, with the realization that $p_m = p_0$, yields for the upstream ($x = 0$) and downstream ($x = l$) surfaces as before[2]

$$a_{10}^m = a_{10}^s \tag{4}$$

$$a_{1l}^m = a_{1l}^s e^{-V_1(p_0 - p_l)/RT} \tag{5}$$

HOLLOW FIBERS: AN UNSUPPORTED MEMBRANE

Fine, hollow fibers as depicted in Figure 2 are employed in reverse osmosis. In principle, the pressurized feed solution may be inside or outside of the bore. The fiber wall serves as the membrane, and no mechanical support such as the porous plate in flat membranes is provided in the simplest case. The membrane pressure here is more difficult to ascertain since the simple arguments used for flat membranes are clearly inadequate. The elastic character of the fiber wall is directly involved since the lack of support and this geometry require the membrane material itself to resist the impressed force. We will obtain the membrane pressure from solutions to the elasticity equation which give the components of the stress tensor σ.

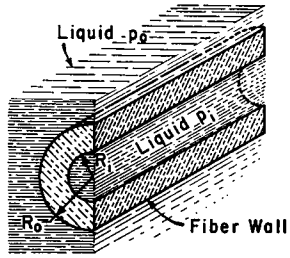

Fig. 2. Hollow fiber geometry.

The components σ_{rr}, $\sigma_{\theta\theta}$, σ_{zz} can then be used to compute p_m via eq. (3). For this purpose, we will treat the hollow fiber of Figure 2 as a long, thick-walled tube with pressures p_i inside and p_0 outside. Further, it is assumed that the fiber wall is isotropic and displays linear elastic behavior. An exact solution to the elasticity equation for this situation is available.[7] The σ_{rr} and σ_{zz} components (tension is positive) at any radial position r are

$$\sigma_{rr} = -\frac{p_0R_0^2 - p_iR_i^2}{R_0^2 - R_i^2} + \frac{R_0^2R_i^2\,(p_0 - p_i)}{r^2(R_0^2 - R_i^2)} \tag{6}$$

$$\sigma_{\theta\theta} = -\frac{p_0R_0^2 - p_iR_i^2}{R_0^2 - R_i^2} - \frac{R_0^2R_i^2(p_0 - p_i)}{r^2(R_0^2 - R_i^2)}. \tag{7}$$

The component σ_{zz} depends on the axial restraints but does not depend on r in any event. Owing to the opposing signs in the position-dependent parts of eqs. (6) and (7), the sum of σ_{rr} and $\sigma_{\theta\theta}$ is independent of this position. Thus, in view of the nature of σ_{zz}, p_m is a constant throughout the fiber wall although two of the stress components do vary.

The magnitude of p_m is unspecified until the exact configuration of the hollow fiber is defined. Many module designs employ a looped-end configuration,[8] and discussion will be based on this geometry. A simple force balance for the looped construction yields

$$\sigma_{zz} = -\frac{p_0R_0^2 - p_iR_i^2}{R_0^2 - R_i^2}. \tag{8}$$

Combining eqs. (6) through (8) in the fashion dictated by eq. (3) gives for p_m

$$p_m = \frac{p_0R_0^2 - p_iR_i^2}{R_0^2 - R_i^2}. \tag{9}$$

For the isotropic, dense-walled, hollow fiber, the membrane pressure is independent of position within the wall, but in general is not equal to either p_0 or p_i. Figure 3 shows a dimensionless plot of eq. (9) as a function of the ratio of the wall thickness, $t = R_0 - R_i$, to the outside radius. For very thick-walled fibers, p_m approaches p_0, while for very thin-walled fibers it becomes very large. The latter case would describe a tubular membrane without support. For the more common case of external pressurization,

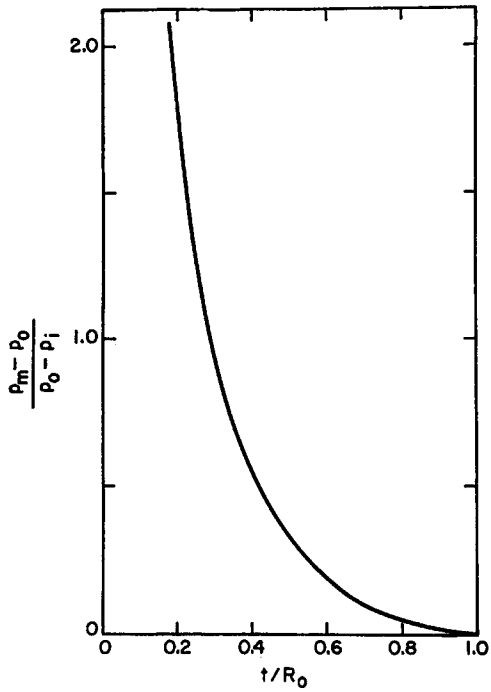

Fig. 3. Reduced membrane pressure for hollow fiber. Wall thickness $t = R_0 - R_i$.

$p_0 > p_i$, the membrane pressure is greater than p_0, while for internal pressurization, $p_i > p_0$, and it may even be negative.

The foregoing analysis is inapplicable for many commercially utilized hollow fibers since the inherent assumption of isotropy is not met. Often the fiber wall is not totally dense throughout but has a gradation of porosity. In many respects such fibers resemble the structure of Loeb-type flat membranes. Generally, there is a totally dense skin which is responsible for the rejection characteristics of the hollow fiber in reverse osmosis. The porous matrix is present merely for mechanical support. Since the matrix is not homogeneous, it is possible to have a different pressure within the solid phase than the liquid contained in the pores. Transport in this region may be regarded as simple viscous flow through the pores. Fluid pressure may be transmitted through the pores up to the skin (a sharp demarcation may not exist) in much the same fashion as with the porous support plate in the flat membrane (see Fig. 1). Equations (6) through (8) are inappropriate for this situation. The mechanical condition within the skin is actually a complex composite of the flat supported membrane and the dense hollow fiber. It therefore seems reasonable that the membrane pressure within the skin would still be independent of position; however, it cannot be computed from any of the arguments given here.

Even a totally dense, hollow fiber may not meet the condition of isotropy, since in reverse osmosis operation there will be a concentration gradient of the solvent (and solute) across the wall. Undoubtedly, the modulus of the fiber wall will depend on the liquid content. This may lead to a variation of p_m with position, but this variation is only a secondary effect. To a good approximation, we may conclude that the membrane pressure is constant throughout the wall of a hollow fiber where diffusive transport occurs, i.e., that portion which is one phase.

THE PRESSURE-INDUCED CONCENTRATION GRADIENT

From the outset it was stated that the action of the applied pressure is to induce a concentration gradient of the solvent when solution-diffusion is the operative mechanism. In this section we will consider in detail how this occurs within the framework of the membrane pressure concept.

For a given membrane and solvent, there is a unique relation between the concentration of solvent and the activity of the solvent in the membrane, a_1^m, when the definition implicit in eq. (1) is used. Once the membrane pressure is known, eq. (2) may be applied at each surface to determine the activity just inside the membrane there. From the activity–concentration relationship, the concentration differential may be determined directly. Equations (4) and (5) give the activities for the special case of the supported membrane. Since for hollow fibers the membrane pressure does not correspond to either fluid pressure, the activities at both surfaces within the membrane will differ from the liquid-phase activities.

We will examine further the special case where the connection between the activity and concentration follows the notion of an ideal solution, since this approach is employed in many situations[7] with some justification. By definition,

$$a_1^m = \frac{v_1}{v_1^*} = \frac{c_1}{c_1^*} \tag{10}$$

where v_1 is the volume fraction and c_1 is the mass concentration of species 1. The asterisk (*) denotes the equilibrium solubility of species 1 in the membrane material. Thus, at an interface where the liquid pressure is p and the membrane pressure is p_m, eqs. (2) and (10) combine after taking the logarithm of both sides to give

$$\ln \frac{c_1}{c_1^*} = \ln a_1^s + \frac{V_1}{RT}(p - p_m). \tag{11}$$

If c_1 is never much different from c_1^*, we may use the approximation

$$\ln \frac{c_1}{c_1^*} \cong \frac{c_1 - c_1^*}{c_1^*}. \tag{12}$$

Combining eqs. (11) and (12) for an upstream surface u and a downstream surface d gives

$$c_{1u} = c_1^*\left[1 + \ln a_{1u}^s + \frac{V_1}{RT}(p_u - p_m)\right] \tag{13}$$

and

$$c_{1d} = c_1^*\left[1 + \ln a_{1d}^s + \frac{V_1}{RT}(p_d - p_m)\right]. \tag{14}$$

The concentration difference then is

$$c_{1u} - c_{1d} = \frac{c_1^* V_1}{RT}\left[(p_u - p_d) - (\pi_u - \pi_d)\right] \tag{15}$$

making note of the definition of osmotic pressure,

$$\pi = -\frac{RT}{V_1}\ln a_1^s.$$

Equation (15) is a familar result[1]; however, the following points are noteworthy. While a linear relation is predicted between Δc_1 and the net pressure, this linearity may break down in extreme situations, even for ideal solutions, owing to the approximation assumed in eq. (12). Further, c_1^* will be affected by the presence of solutes in the liquids, and thus a different value for this quantity may be required in eq. (13) than eq. (14). In general, solutes will cause the membrane to deswell and thereby reduce the flux below that for pure solvent at the same net pressure, $\Delta p - \Delta\pi$. It is to be noted that this membrane pressure does not appear in the final result, i.e., eq. (15), because it cancels out in the subtraction of eq. (14) from eq. (13). This cancellation occurs only as a result of the linearity of these relations, and it is our contention that it is only because of this condition that the role of membrane pressure has been successfully ignored in the past.

It is also important in the formulation of eq. (15) that the membrane pressure be constant throughout the membrane. The total decrease in the chemical potential of solvent going from the upstream liquid to the downstream liquid is $V_1[(p_u - p_d) - (\pi_u - \pi_d)]$, regardless of what occurs within the membrane. If p_m is constant, all of this decrease occurs within the membrane via the concentration gradient. If p_m varies, the gradient is altered. If, in fact, p_m were p_u at the upstream surface and p_d at the downstream surface, there would be no gradient at all. A recent determination of the concentration gradient in a highly swollen, flat, supported membrane showed that the entire decrease in chemical potential could be accounted for by the concentration gradient.[3] Also in this case, identification of the membrane pressure was required to describe the induced concentration gradient, thus confirming the importance of this parameter for a complete description of the solution-diffusion process.

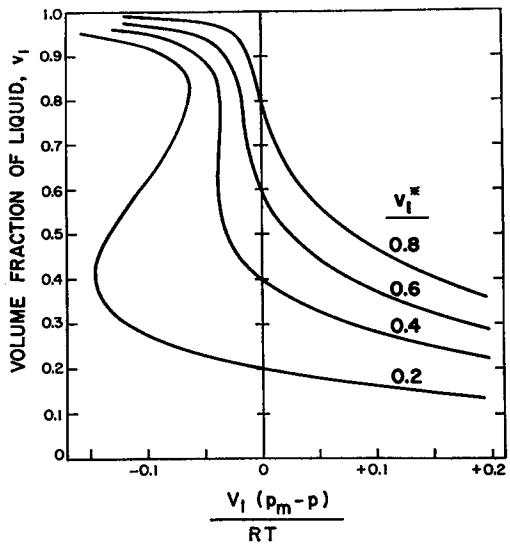

Fig. 4. Equilibrium swelling of a crosslinked polymer network where the pressure in the polymer, p_m, and the surrounding liquid, p, are different. Calculations are for $(\nu_e/V_0)V_1 = 10^{-2}$. Note that at a reduced abscissa of 0.1, $p_m - p = 330$ and 1650 psi for $V_1 = 100$ and 20 cc/mole, respectively.

In general, the relation between c_1 and $p - p_m$ is not linear since the ideal solution concept is not universal. We will pursue for illustrative purposes the special case of a crosslinked polymer–solvent system which obeys the Flory-Huggins mixing theory, with elastic effects accounted for by the theory of rubber elasticity. Swelling is restricted to one direction after equilibrium at $p = p_m$ is obtained. No solute is considered. The relation between the liquid volume fraction v_1 and $p - p_m$ is[1]

$$\ln a_1^m = \frac{V_1(p_m - p)}{RT} = \ln v_1 + (1 - v_1) + \chi_1(1 - v_1)^2 + V_1 \frac{\nu_e}{V_0}\left[\frac{(1 - v_1^*)^{1/3}}{(1 - v_1)} - \frac{(1 - v_1)}{2}\right]. \quad (16)$$

This relation is plotted in Figure 4 for four arbitrarily chosen values of v_1^* which is the equilibrium volume fraction of liquid in the network at free swelling, i.e., $p_m = p$. In all cases, the relation is nonlinear but becomes more nearly so at positive values of $p_m - p$ at low swelling. For values of $v_1^* < 0.2$, a linear approximation would be justified for most purposes. Plots such as these have been employed in the past[2,3,9] for positive values of $p_m - p$ with considerable success. It is to be recalled that at the downstream membrane surface in a flat, supported membrane, $p_m - p = p_0 - p_t$. Figure 4 extends into the region of negative $p_m - p$, which is never encountered with flat, supported membranes (at the upstream surface $p_m - p = 0$), but this region would be encountered with internally pressurized,

hollow fibers according to the prediction given in Figure 3. For this system under discussion, nonlinearities are quite evident in this region. In fact, for $v_1^* = 0.2$ and 0.4, v_1 appears to become double-valued at high negative pressure differentials. This strange state of affairs is simply an indication of a thermodynamic transition where at a point two phases develop: one rich in polymer, the other rich in solvent. In other words, for p_m sufficiently less than p, the poorer solvent "dissolves" the membrane. To the author's knowledge, no transition such as this has ever been reported. However, it is to be noted that p_m can only be made less than p by applying a tensile stress field to the polymer, and it is doubted whether it is mechanically possible to reach a stress sufficient to cause this change because of strength limitations of the material.

SUMMARY

It has been proposed here that the membrane pressure is a necessary consideration in the total formulation of solution-diffusion models for solvent transport in reverse osmosis. For some purposes it may be ignored, depending on the swelling characteristics of the membrane. However, the necessity of its use in all formulations for highly swollen membranes has been established.[2,3] The value of the membrane pressure for supported, flat membranes may be reasoned from rather simple arguments. In the case of hollow fibers, this quantity was assumed to be given by eq. (3), which is a rational assumption but largely unproven. The results of this hypothesis do, however, lead to the appealing conclusion that p_m is constant across the fiber wall.

Some further discussion of the use of the mechanical definition of p_m in eq. (3) as a thermodynamic variable is in order. This equation predicts the pressure within a material subjected to an externally applied uniaxial stress of S_{11} is $-{}^1/_3\, S_{11} + p$, where p is ambient pressure. Therefore, $p_m - p$ will be positive if this stress is compressive and negative if tensile. It would thus be informative to know what happens to the level of swelling of this material when immersed in a solvent and subjected to stressing. Treloar[10] and Flory and Rehner[11] have reported such experiments with cross-linked rubber immersed in solvents. For tensile stressing, the swelling, i.e., v_1, increases, whereas it decreases for compression loading. These directions are consistent with the general prediction of eqs. (3) and (2) and the special case shown in Figure 4. The published experiments are inadequate to test the quantitative use of eq. (3) as a predictor for these responses, although suggestions to this effect have been made.[12,13]

In this paper we have presumed from the outset to treat the transport of liquids through a nonporous polymer membrane which occurs by a solution-diffusion mechanism when the concentration-gradient driving force is created by the application of a pressure *differential* across the membrane. From theoretical reasoning and experimental results, we conclude that in the ideal case, liquid transport in reverse osmosis occurs without any pressure gradient within the membrane. The pressure we speak of should be

consistent with both thermodynamics and mechanics and must be considered to act on the continuum and not individual species. Other points of view exist in the literature. For example, Fatt et al.[14] consider that when a liquid swells a membrane, an "imbibition" pressure is generated and that when a gradient of swelling exists, there is a gradient of "imbibition" pressure. He goes on to consider that the flux of liquid under these conditions consists of two parts: one is a diffusive flux driven by the gradient of liquid concentration and the other is a convection flux driven by the "imbibition" pressure gradient. Fatt's "imbibition" pressure is identical in definition to Gehman's "swelling" pressure, and both are effectively defined by eq. (2). Except under certain conditions, e.g., at surfaces or when the membrane is in equilibrium throughout, the "imbibition" pressure Fatt uses is a useful but hypothetical concept. When applied to a point in the interior of a membrane with a swelling gradient, this pressure (when calculated from the solvent activity at that point) (a) is not the pressure felt by the continuum at that point nor (b) does it properly give the chemical potential of the liquid when inserted into eq. (1). From this point of view we can see no basis for considering this factor capable of driving a convective flux.

Bert[15] considered a similar convective transport mechanism as described above to explain the curvature in plots of water flux versus applied pressure, referred to by Bert as "compaction," for a presumably totally dense cellulose acetate membrane. We feel that such a curvature can occur for three reasons when solution-diffusion mechanisms are operative: (a) In membranes with a porous matrix below the active skin, a compaction of the matrix may occur at high applied pressures with a resulting decrease in permeability of the composite (this phenomenon is time dependent and is largely irreversible). (b) The thermodynamics may be such that a nonlinear relation between the induced concentration differential and the applied pressure exists.[2,3] (c) The diffusion coefficient may vary with concentration in such a way as to produce this effect. The latter two may exist in totally dense membranes without any porous matrix, and they are time independent and reversible. Bert's analysis considers that there is a gradient of pressure and that the pressure at each point reduces the swelling there according to the concept of the "imbibition" pressure. The curvature he predicts arises from the dependence of the transport coefficient employed on swelling level. The profile of water content that he predicts is one of equilibrium swelling at the *downstream* or low-pressure surface and a *reduced* swelling at the upstream or high-pressure surface, which is the exact opposite of our earlier prediction.[2] The result gives a water concentration gradient in the opposite direction of the water flux and is in direct conflict with all experimental attempts to measure this gradient in reverse osmosis.[3,16]

This work was supported by the National Science Foundation and the Bureau of Engineering Research at the University of Texas. The aid of O. M. Ebra-Lima through discussions and calculations is gratefully acknowledged.

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Received July 27, 1971
Revised October 26, 1971