**Separation Science and Technology**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

# Mechanisms of Transport through Reverse Osmosis Membranes

M. A. Mazid[a][b]
[a] DIVISION OF CHEMISTRY, NATIONAL RESEARCH COUNCIL OF CANADA, OTTAWA, CANADA [b] Export Packers Company Ltd., Science and Technology Centre, Winnipeg, Canada

**To cite this Article** Mazid, M. A.(1984) 'Mechanisms of Transport through Reverse Osmosis Membranes', Separation Science and Technology, 19: 6, 357 — 373
**To link to this Article: DOI:** 10.1080/01496398408060657
**URL:** http://dx.doi.org/10.1080/01496398408060657

SEPARATION SCIENCE AND TECHNOLOGY, 19(6 & 7), pp. 357-373, 1984

# REVIEW

# Mechanisms of Transport through Reverse Osmosis Membranes

M. A. MAZID*

DIVISION OF CHEMISTRY
NATIONAL RESEARCH COUNCIL OF CANADA
OTTAWA, ONTARIO, CANADA K1A 0R9

## Abstract

Reverse osmosis membrane transport mechanisms are briefly reviewed. There are several approaches which basically involve pore flow and/or diffusive flow. At one extreme, as in the solution–diffusion model, there is no clear-cut route for the transport, while others, like the preferential sorption–capillary flow mechanism, invoke definite pores and capillaries. The fundamental concept of interfacial adsorption combined with mass transport through the capillaries, which led to the development of asymmetric porous membranes, are the prominent features of the latter mechanism. This has been developed further to enable specification and prediction of performance of a membrane in terms of average pore size and its distribution. A quantitative description of penetrant solution and diffusion in microheterogeneous media as described by the dual sorption theory and a mechanism based on irreversible thermodynamics are also discussed. The usefulness and limitations of various approaches are pointed out.

## INTRODUCTION

Membrane separation processes are as old as any living organisms, but it is only during the last two decades that membranes have emerged from being a subject of laboratory research to commercial applications in medicine and industry. The use of reverse osmosis for water desalination in particular has been increasingly studied, and a considerable amount of literature is available with respect to some typical water treatment and water pollution control applications. A large number of other potential applications of the technique have been studied in the laboratory and in pilot plant scale using

---

*Present address: Export Packers Company Ltd., Science and Technology Centre, 70 Irene Street, Winnipeg, Manitoba, Canada R3T 4E1.

0149-6395/84/1906-0357$3.50/0

Loeb-Sourirajan type or similar membranes, but the process has not yet found general acceptance in various separation industries. The current worldwide activity on the subject certainly indicates the growing awareness about the obvious potential of the technique, while there is an apparent lack of interest in a fundamental understanding of "reverse osmosis" itself. It is notable that the practical applicability of this technique has been limited greatly by the availability of a suitable membrane for a particular purpose. The appropriate membrane could, however, be formulated on a rational basis if the mechanism of transport through the membrane is properly understood. This understanding is also important for the concepts of membrane and system specifications and predictability of their performances which are fundamental to reverse osmosis engineering.

There are several approaches toward understanding of the basic mechanisms, and a number of papers have been published in this area. However, most of the approaches fall into one or the other extreme, viz., pore flow and diffusive flow. In the first case, the membrane is considered as a bundle of capillaries where the flow is determined by the application of Poiseuille's equation, while the second picture involves dissolution of the components in the membrane followed by diffusion through the membrane. It has been recognized that the physical structure of the membrane determines the transport behavior in the pore flow, whereas the solute–polymer and the solvent–polymer forces together with the chemical structure of the membrane material are the dominant factors in diffusive flow. In either of these approaches, however, no attention is being paid to the interface between the fluid mixture and the solid membrane. The fundamental concept of interfacial adsorption which led to the original development of asymmetric membranes has been neglected or ignored. This feature has prominence only in the preferential sorption–capillary flow mechanism proposed by Sourirajan (*1*). Several workers also made use of irreversible thermodynamics to reverse osmosis separations. An extensive review of reverse osmosis membranes and transport models has been published recently (*2*). However, it is the purpose of this article to briefly survey the principal approaches and to discuss their usefulness.

## PREFERENTIAL SORPTION—CAPILLARY FLOW MECHANISM

This mechanism was developed by Sourirajan (*1*) following a suggestion made by Yuster in 1956 that an aqueous solution of sodium chloride in contact with a solid membrane of appropriate chemical nature can give rise to a multimolecular layer of deionized water, which in turn offers a potential means of separating fresh water from the bulk of the solution. The thickness of the fresh water layer at the interface can be calculated on the basis of Gibbs adsorption equation, and it has been found that this thickness is in fact only of the order of a molecular layer. However, the Gibbs equation shows that the thickness of this layer depends on the variation of the interfacial tension with the activity (concentration) of the salt in solution. Hence, the nature of the solution as well as that of the surface in contact are important in this regard. This feature has been incorporated into the "preferential sorption–capillary flow" mechanism according to which reverse osmosis separation is the combined result of preferential sorption of one of the constituents of the feed solution at the membrane–solution interface, and mass transport by fluid permeation under pressure through the capillaries of the microporous membrane. An appropriate chemical nature of the membrane surface as well as the physical structure in terms of the appropriate number and size of the pores are essential for the practical success of this separation process. It is important to note that the term "preferential sorption" was used to describe the existence of a steep concentration gradient at the membrane–solution interface, and the terms "pore" and "capillary" refer to any void space connecting the high pressure and the low pressure side of the membrane.

One of the most fundamental aspects of this mechanism is the physicochemical criteria governing the preferential sorption at the interface. These criteria have been identified in terms of the solute–solvent–membrane material interactions arising from polar (hydrogen bonding), steric, nonpolar (hydrophobic), and/or ionic character of each of the above components. All these interactions can be expressed quantitatively and separately, but the net result determines whether solute or solvent (or neither) is preferentially sorbed, and hence govern the relative separation of the constituents which may be positive, zero, or even negative. The mechanism also tells that reverse osmosis is fundamentally not limited to any particular solvent, solute, membrane material, level of solute separation and that of solvent flux, or operating conditions of the experiment. With an appropriate material for the membrane, it is possible to obtain any degree of solute separation simply by changing the average pore size and the operating conditions. Besides, a particular membrane can give different levels of solute separation for different solutes due to differences in preferential sorption and mobility of the preferentially sorbed species through the pores. The existence of a critical pore diameter for maximum solute separation and fluid permeability is recognized for each system, and it is postulated that there could be no flow of interfacial liquid by this mechanism through the membrane if there are no pores at all. The mechanism also predicts concentration-dependent salt permeability since the thickness of the salt-free layer (preferentially sorbed layer) depends on concentration.

The mechanism gives rise to a set of basic equations relating to pure water permeability constant, $A$, the transport of solvent water, $N_B$, the solute transport parameter, $(D_{AM})/K\delta$, and the mass transfer coefficient, $k$, as follows:

$$
\begin{aligned}
A &= (\mathrm{PWP})/(M_B \times S \times 3600 \times P) \\
N_B &= A[P - \Pi(X_{A2}) + \Pi(X_{A3})] \\
&= \left(\frac{D_{AM}}{K\delta}\right)\left(\frac{1 - X_{A3}}{X_{A3}}\right)(c_2 X_{A2} - c_3 X_{A3}) \\
&= kc_1(1 - X_{A3}) \ln\left(\frac{X_{A2} - X_{A3}}{X_{A1} - X_{A3}}\right)
\end{aligned}
$$

where PWP = pure water permeability, $M_B$ = molecular weight of water, $S$ = membrane area, $P$ = operating pressure, $\Pi$ = osmotic pressure, $X$ = mole fraction, and $c$ = molar density of solution, the subscripts 1, 2, and 3 being referred to the bulk feed solution, concentrated boundary solution, and the membrane permeated product solution, respectively. The transport analysis (*3*) is based on the fact that PWP is directly proportional to the operating pressure, the solvent water transport ($N_B$) through the membrane is proportional to the effective pressure, the solute transport ($N_A$) through the membrane is due to pore diffusion through the membrane capillaries and hence proportional to the concentration difference across the membrane, and the mass transfer coefficient $k$ on the high pressure side of the membrane is given by the "film" theory on mass transport. In this analysis, $A$ is a fundamental quantity which is a measure of the overall porosity of the film. This corresponds to the condition of zero concentration polarization and is independent of any solute under consideration. The parameter $(D_{AM}/K\delta)$ plays the role of a mass transfer coefficient with respect to solute transport through the membrane. This is a combination of several interrelated factors but can be treated as a single quantity to a good approximation. The values of $A$, $(D_{AM}/K\delta)$, and $k$ for any system can be calculated from a single set of experimental pure water permeability, product rate, and solute separation data. The first two quantities can specify a membrane at a given operating pressure while the performance of the membrane can be predicted if the mass transfer coefficient applicable for the high pressure side of the membrane is known. Based on the same experimental quantities, it has also become possible to specify and predict the performance of a system. Sourirajan (*4*) states that "this mechanism is consistent with all known experimental facts on reverse osmosis; it immediately directs attention to the existence of the science of reverse osmosis; and it offers a rational basis for the useful development of the science of reverse osmosis in all its aspects." Thus, the preferential sorption–capillary flow mechanism appears to be of significant usefulness while the concepts have yet to gain entry into the field of reverse osmosis engineering.

## MECHANISMS INVOLVING DIFFUSION

A number of models for transport through reverse osmosis membranes have been proposed in terms of diffusive flow. Among the earlier workers, Reid and Breton (*5*) considered that the transfer of water and ions through cellulose acetate membranes is governed by two different types of diffusion, viz., that the ions and molecules which can associate with the membrane through hydrogen bonding are transported by alignment-type diffusion while those that cannot enter into hydrogen bonding are transferred by hole-type diffusion. Arguments were based on the transient occurrence of pores, due to Brownian motion, which permit ion transport in these regions, and on the structural similarity between the bound water in cellulose acetate and in ice. These hypotheses were rejected by Lonsdale and co-workers (*6*) who believe that reverse osmosis separation is governed by a solution–diffusion mechanism. According to these workers, the solute and the solvent dissolve in the membrane material and then permeate through the membrane by diffusion through the homogeneous nonporous surface layer.

Transport equations based on the solution–diffusion model have been derived (*7*). The water flux, $J_1$, is given by the equation

$$J_1 = \frac{D_1 C_1 \bar{V}_1}{RT}\left(\frac{\Delta P - \Delta \Pi}{\Delta \chi}\right) = A(\Delta P - \Delta \Pi)$$

where $D_1$ = diffusion coefficient for water in the membrane, $C_1$ = dissolved water concentration in the membrane, $\bar{V}_1$ = partial molar volume of water in the external phase, $\Delta P = P' - P''$ and $\Delta \Pi = \Pi' - \Pi''$ are the applied pressure difference and the osmotic pressure difference, respectively, across the membrane, and $\Delta \chi$ = membrane thickness. Here the prime and the double prime refer to the feed and the permeate, respectively. The quantity $A$ is a measure of the water flux per unit net pressure, having dimensions in $\mathrm{g/cm^2 \cdot s \cdot atm}$, and is a characteristic of the membrane which has been referred to as the "membrane constant."

The salt flux, $J_2$, through an "imperfection-free" membrane in the case of large concentration differences, is given by

$$J_2 = D_2 K \Delta \rho_2 / \Delta \chi = B \Delta \rho_2$$

where $D_2$ = diffusion coefficient for salt in the membrane, $K$ = distribution coefficient for salt between membrane and solution, and $\Delta\rho_2 = \rho_2' - \rho_2''$ = difference in salt concentration in the solution on the two sides of the membrane. The quantity $B(= D_2K/\Delta\chi)$ was termed the "solute permeation constant."

Finally, the salt rejection, $S$, is defined by the equation

$$S = (\rho_2' - \rho_2'')/\rho_2'$$

Now, since the concentration of the salt in the permeate is determined by the realtive fluxes of water and salt, it is given by

$$\rho_2'' = J_2\rho_1''/J_1$$

Thus,

$$S = 1 - \frac{J_2\rho_1''}{J_1\rho_2'} = \left[1 + \frac{D_2KRT\rho_1''}{D_1C_1\bar{V}_1(\Delta P - \Delta\Pi)}\right]^{-1}$$

This equation was used to predict the salt rejection as a function of the applied pressure and the salt concentration of the feed. A definite theoretical level of solute separation was calculated, but in practice the salt rejections were found to be lower, and the discrepancy was supposed to be the result of membrane imperfection.

A linear relationship between water flux and net pressure as predicted by the theory was obtained with "dense membranes" and in short-term experiments with modified membranes. The decline of water flux through modified membranes after long runs at high pressure was believed to be the result of compaction of the porous substructure. This was considered to be a serious problem in practice, and Riley et al. (*7*) tried to justify the search for a "perfect membrane." They were able to improve the salt rejection significantly, but the flux was still a function of pressure, indicating that a significant fraction of the salt flow was strongly coupled to the water flow or, alternatively, that the imperfections were not sealed off. Finally, it was found possible by using immaculate techniques to prepare thin films that were apparently free from imperfections and with which theoretical salt rejection was achieved.

In a later study, Lonsdale et al. (*8*) used modified cellulose acetate membranes which were considered to be of finely porous structure, and measured the rejection of some organic and inorganic solutes. The intrinsic permeability of the membranes to the solutes was also measured by a desorption-rate method in a way that does not depend on film perfection. The possibility of the specific interactions between water and membrane, solute and membrane, and water and solute within the membrane was mentioned. The last interaction, usually referred to as flow coupling, was treated in some detail but this was also considered unimportant on the basis of agreement between the intrinsic permeability data and those from the reverse osmosis experiments. Nevertheless, it was concluded that "the intrinsic permeability of the solute rejecting skin to water and solutes is much higher with these membranes, and one might expect that the solution–diffusion model would be of limited usefulness." The reason is obvious, that the real membranes are not the so-called "perfect" or "homogeneous" membranes.

One particular comment can be made on the usefulness of the solution–diffusion model. The membrane constant $A$, defined in the equation for water flux, is not really a constant since it necessarily depends on the nature of the solute, its concentration in feed solution, and other feed flow conditions. Similar remarks can be made for the solute permeation constant $B$. Hence, the specifications by the quantities $A$ and $B$ obtained from a single set of experimental data for any membrane together with the equations for solvent and solute fluxes are not sufficient to predict solute separation and membrane flux obtainable with that membrane for any feed concentration and any feed flow condition.

There are other workers who also favor some kind of diffusive mechanisms even with real membranes. Thus, Michaelis et al. (*9*), using Loeb-Sourirajan type membranes, found it necessary to introduce in their model a transitional flow which is intermediate between purely activated diffusion through consolidated polymer and unrestricted pore flow. It was described as a hydrostatic stress-biased diffusion of salt in partially restricted pores, while the water transport was considered to occur predominantly by molecular diffusion through the polymer matrix.

Banks and Sharples (*10*) developed equations to describe pore flow and diffusive flow showing quantitative relations between salt rejection and pressure. They were able to justify partial rejections at pressures below the osmotic pressure of the influx solution by both mechanisms, and showed that rejection increases continually as soon as the pressure is increased and can approach 100%, especially by diffusive flow. It was also noted that separation can occur in a membrane which is free from pores, if solvent and solute both permeate by a true solution/diffusion process, provided that solute is present in low concentration, and that sufficiently high driving pressures are used to swamp solute flow by solvent flow. Banks and Sharples were aware of the build-up of a boundary layer concentration but avoided this aspect just by saying that "steps are invariably taken in current research in this field to minimize the effect, e.g., by stirring at the membrane surface."

Furthermore, the possibility that pores may contribute to the flow of solute was excluded on the ground that at high pressures when the limiting rejection is obtained, this limiting value would be expected to be less than 100% because, although desalinated water would permeate the pore-free areas at a rate which increases with pressure, the salt being forced through the pores would also increase with pressure in a similar way, so that no process of rejection would be obtained. However, the fact that rejection as high as 99.67% was obtained at 1500 psi for some salts was used to invalidate the possibility of any pore flow that might be expected at low pressures. Thus, it was concluded that the transport mechanism in reverse osmosis is one of diffusive flow through the pore-free layer in the membrane.

The possibility that both types of flow may be involved in the mechanism has been recognized by Sherwood et al. (*11*) who propose the model of transport by the parallel processes of diffusion and pore flow. These workers used a rotating cylindrical membrane to minimize the effect of concentration polarization of salt in the solution adjacent to the membrane, supposedly due to water flux to and through the membrane. This is not in accordance with the basic requirement of the negative adsorption of salt as described by the preferential sorption–capillary flow mechanism. In either case, however, the product salt concentration would vary much more than the product water rate as concentration polarization is reduced by increasing the rpm, whatever may be the mechanism of transport.

## IRREVERSIBLE THERMODYNAMICS AND OTHER MECHANISMS

The thermodynamic approach to the problem of permeability of membranes also concerns the nature of diffusion. In the case of free diffusion, solvent and solute migrate only relative to each other, and it is generally known that the hydrodynamic resistance to diffusive flow is due to the friction between solute and solvent alone, so that diffusion in a solution of a single solute is determined by a single diffusion coefficient. The passage through a membrane has been considered by Kedem and Katchalski (*12*) to involve two additional factors, namely, the friction between solute and membrane and the friction between solvent and membrane. A full description thus has to take account of three coefficients whose values will depend on the nature of the three processes involved.

Kedem and Katchalski pointed out that the conventional description of transport through membranes make use of two equations, one for solute flow and one for volume flow. These equations are generally based on two permeability coefficients—the solute permeability coefficient and the water permeability coefficient—and are therefore incompatible with the requirements of the thermodynamics of irreversible processes. The inconsistencies were removed by a thermodynamic treatment which led to a three coefficient system taking into account the solute–solvent, solute–membrane, and solvent–membrane interactions. It was also shown how the pertinent coefficients may be derived from the experimental data, and how to choose suitable conditions in order to obtain all the required information on the permeability of the membranes. In this approach, coupling of solute and solvent flow was included as an independent parameter. Spiegler and Kedem (*13*) assumed constancy of the three coefficients, termed the specific hydraulic permeability, the local solute permeability, and the reflection factor, the third one being said to be a quantitative measure of solute separation. They derived transport equations theoretically applicable for the entire 0 to 100% range of separation, and their validity has been demonstrated experimentally by Jagur-Grodzinski and Kedem (*14*).

Transport equations based on nonequilibrium thermodynamics have been derived by other workers, but they do not generally deal with the real membranes. Of particular relevance to our interest is the recent work based on the thermodynamic approach by Castillo (*15*). He derived an equation which gives the flux of a solvent through a cellulose acetate membrane under an operating pressure $P$ and an effective pressure $\Delta P = P - \Delta\Pi$, where $\Delta\Pi$ is the osmotic pressure of the system.

Following Sourirajan (*1*), the solvent transport was supposed to consist of two contributions: one of viscous flux through the pores and another due to capillary–sorption flux produced by the hydrogen–polymer bonds. Both fluxes were considered basically proportional to the effective pressure, and the total solvent flux was given by

$$J = (K_1^{-\alpha P} + K_2)\Delta P$$

where $K = K_1 + K_2$ corresponds to a permeability coefficient which depends on the dimensions, structure, and chemical composition of the membrane. In deriving this expression, the deformation effect of pressure $P$ over the membrane was also considered, and $\alpha$ was termed the compressibility coefficient. It is interesting to note that Sourirajan and co-workers (*16–19*) also described earlier the solvent flux by an empirical relationship which shows the same dependence with the pressure, but in which $\alpha$ is represented by the reciprocal of the maximum operating pressure. Castillo, however, interprets $1/\alpha$ as a pressure at which the viscous flux diminishes to 63% of its initial value.

An expression for solute rejection was derived by Castillo using the phenomenological Onsager equations as a theoretical basis. The solute flux was also assumed to be due to two combined driving forces, viz., a concentration gradient and the effective pressure $\Delta P$. The concentration gradient flux followed a Fickian type of diffusion model, and the pressure flux was represented by a coupling effect with the solvent. The final expression for the solute rejection factor was given by

$$f = \frac{a^1 \Delta P}{b^1 \Delta P + 1}$$

where $a^1$ and $b^1$ are constants which were defined in terms of solution properties and phenomenological coefficients. This equation was tested by experimental results showing linear plots of $1/f$ against $1/\Delta P$. Castillo et al. (*20*) further gave an explanation of the basic principles of preferential sorption of solvent and negative adsorption of solute using electrodynamic concepts.

There are other approaches recognizing the fundamental aspects of the preferential sorption–capillary flow mechanism. Glueckauf (*21*) applied the principles of electrostatics and made use of the Born equation to show that work is necessary to bring an ion toward the membrane material of low dielectric constant. This work is translated into the repulsive force for the ion, giving rise to a layer of pure water at the membrane–solution interface, and therefore positive solute separation is obtained with ionic solutes. Glueckauf further pointed out that the above repulsive forces are much larger at the interior of a pore than at the plane surface. He derived an expression which relates the solute separation with pore radius, ionic radius, ionic charge, feed concentration, and dielectric constants. The predictions were found to be qualitatively consistent with results for many inorganic electrolytes in aqueous solutions and porous cellulose acetate membranes. However, the results were based on calculated values of boundary concentrations of the feed solution, and the agreement between the experimental data and the calculated separation data were especially poor at higher feed concentrations. The inadequacy of the treatment could be due to the fact that the number of pores and the pore size distribution were not taken into account. The role of dielectric constants was emphasized, but this could not be the only criteria governing solute separation. However, the analysis provides at least a partial answer regarding the physicochemical criteria of preferential sorption at the membrane–solution interface.

Glueckauf's predictions were also confirmed explicitly by Beans' (*22*) analysis of diffusion through pores based on electrostatic forces which cause ions to avoid a region of low dielectric constant. Again, the importance of a low dielectric constant for the choice of the membrane material and the governing significance of the ionic valency on electrostatic repulsion and solute separation in reverse osmosis were illustrated. It is noted that the equations of Gleuckauf and Bean were derived for neutral membrane surfaces, and these were found to apply equally for the separation of ionized organic solutes. In the case of a charged membrane, additional effects due to the setting up of an electrical double layer at the membrane–solution interface are expected. Other factors such as electrostatic shielding by oppositely charged ions or ion pairing, and pore geometry cannot be neglected.

The theory of Dytnerskii et al. (*23*) is also based on the assumption that the surface of a reverse osmosis membrane contain capillary pores of various sizes. It suggests that a lyophilic membrane in contact with an aqueous solution can give rise to an equilibrium layer of bound water formed on the membrane surface and the walls of the capillaries. The ions are hydrated and cannot be transported through most of the capillaries because of their size limitations. However, the thickness of the bound water layer can be decreased by the application of pressure, and liquid can flow through the capillaries, disrupting the initial equilibrium. The equilibrium would subsequently be reestablished due to the interaction of the membrane with the hydrate envelopes of the nearby ions which are partially dehydrated. Thus, the extent of reverse osmosis separation depends on the degree of dehydration of ions or the strength of the hydrate envelope of the ions, which in turn depends on the ion–solvent and membrane–solvent interactions. It was found that the strength of the hydrate envelope of ions increases with decreasing crystallographic radii of ions and with an increase in their charge. In order to fit the experimental data, however, some correction factor which characterized the asymmetry in the position of the water dipole was introduced to the ionic radii.

More recently, a quantitative description of penetrant solution and diffusion in microheterogeneous media has evolved under the name of the "dual sorption theory" (*24*). This theory postulates that two concurrent modes of sorption are operative in a microheterogeneous medium. The nonlinear sorption isotherms can be decomposed into a linear part that accounts for normal dissolution (an ordinary diffusion-controlled sorption described at equilibrium by Henry's law) and a non-linear Langmuir-type part that accounts for immobilization of penetrant molecules at fixed sites within the medium (hole-filling process). The equilibrium part of the theory is simply expressed by the equation for the isotherm as follows:

$$C = k_D p + \frac{C'_H bp}{1 + bp}$$

where $C$ = solubility in the polymeric material, $p$ = pressure, $k_D$ = Henry's law dissolution constant, $b$ = hole affinity constant, and $C'_H$ = hole saturation constant. The first term represents the sorption of normally diffusible species while the second term represents sorption in microvoids or "holes." The hole affinity constant, $b$, represents the ratio of rate constants of sorption and desorption of penetrant in the holes. It should be noted that this theory was originally developed to account for negative deviations from Henry's law behavior exhibited by some simple gases in glassy polymers, but it has also been postulated that the second mode of sorption may be associated with any mechanism which immobilizes penetrant molecules in a microheterogeneous medium. In particular, the theory has been claimed to be successful in reverse osmosis solvent transport.

Vieth and co-workers (*25*) applied this theory to their data with a series of polymers, including hydroxyethyl methacrylate (HEMA), copolymers of HEMA and ethyl methacrylate (EMA), cellulose acetate, cellulose nitrate, and polyurethanes. They observed significantly pronounced solvent clustering due to immobilized solvent which was entrapped at localized sites within the polymer matrix. The degree of clustering was determined directly from sorption isotherms, and the large values obtained were indicative of strong interaction between water and polymer. It was noted that this interaction must have a significant effect on the water transport properties of the membrane. The equation for reverse osmosis water flux was also derived originally under the assumption that the water–membrane equilibrium obeyed Henry's law, and subsequent application of a nonideal equilibrium relationship showed good agreement between the reverse osmosis data and the transient–sorption data. Considerable emphasis was laid on the clustering phenomenon and the effective diffusivities of water. It was concluded that "a simple yet suitable criteria for predicting in advance the potential usefulness of a polymer for reverse osmosis is the value of the water cluster size within it."

The conclusion seems to be attractive but probably an oversimplification because the cluster size would depend on the particular solution, its concentration, and other experimental conditions. Furthermore, it is based on the classical diffusion time-lag data which are difficult to rationalize in terms of the steady-state conditions. Vieth et al. (*24*) nevertheless pointed out that the presence of a mechanism for immobilization should not have any significant effect on the steady-state rate of permeation through the membrane.

## RECENT DEVELOPMENTS IN TRANSPORT MECHANISM

We have discussed the various mechanisms of reverse osmosis transport, many of which were developed during the 1960s. In recent years, a great number of papers and monographs have been published dealing largely with the practical aspect of membrane separations. Several review articles on transport models, notably by Soltanieh and Gill (*2*), Woermann (*26*), and Jonsson (*27*), have appeared, but original studies of fundamental physicochemical aspects have been scanty. Different workers have used one or another of the mechanisms so far discussed to interpret or explain their results, and it appears that further developments in transport mechanisms have somehow depended on the recognition of membrane–solution interfacial or surface forces.

Thus Derjagin et al. (*28*) developed a theory of reverse osmosis separation of solutions, based on the consideration of the effective energy of interaction of solute molecules with the membrane. The approach depends on the concept of convective diffusion of the solute molecules through the potential barrier that is set up by the forces of interaction of solute molecules with the surface of the membrane pores. Effective values of interaction energies for nonelectrolyte solutions have been calculated, and it has been pointed out that the processes taking place "at the inlet in the membrane" play the decisive part in the separation process. The importance of the size of pores in the distribution of the components of the solution over the cross section of the pores, as determined by different components of surface forces, has been discussed, but it has nevertheless been incorporated into the transport analysis.

Neogi and Ruckenstein (*29*) introduced viscoelectric effects in reverse osmosis and solved equations of motion and conservation, which include the effect of the electric field, together with the Poisson equation, for a single charged cylindrical pore. They computed the flow rate of water as well as the fluxes of salt and the rejection coefficient over a wide range of conditions. The calculations were carried out for both constant surface potential and constant surface charge, and it was concluded that a membrane can reject salt only up to a maximum value for a given set of conditions, the maximum being primarily determined by the electrical properties of the pore walls and to a large extent by the diffusivities of the co-ions and counterions. It is apparent that these properties in turn would depend on the size of the membrane pores, but again the role of the pore sizes together with interfacial forces have not been considered explicitly in describing the transport behavior.

In another study of the mechanism of separation of binary aqueous solutions by reverse osmosis, Fomichev and Kochergin (*30*) analyzed solute "retardation" in terms of structural changes of liquid in membrane pores and found that the distance from the surface determines the effect on liquid structure and hence on solute retardation (separation). There were disagreements between experimental and calculated solute rejection which they attributed to the failure to take into account the pore size distribution and the absence of dependence of different coefficients on the distance from the membrane surface.

The importance and significance of pore size and its distribution have been clearly described by the surface force–pore flow model developed by Matsuura and Sourirajan (*31*). In this approach the surface forces acting on the solute are expressed by an electrostatic or a Lennard-Jones type of potential function, and the solute and solvent transport through the membrane under the influence of such forces are expressed through appropriate mass transport equations for an individual cylindrical pore having an average radius and an average effective pore length. This model gives an expression for the ratio of membrane permeated product rate to pure water permeation rate for a given area of membrane surface, which makes it needless to specify explicitly the number of pores involved in the transport. The analysis also results in general expressions for solute separation and fluid flux which are valid for negative or positive adsorption of solute, i.e., for the preferential sorption of solvent or of solute at the membrane–solution interface, as described previously by Sourirajan (*1*). The analytical expressions were derived in detail, and it has been illustrated that the experimental reverse osmosis data are well predicted by the surface force–pore flow model which allows characterization and specification of a membrane precisely in terms of an average pore size and its distribution along with a quantitative measure of surface forces.

The Lenard-Jones type of surface potential function and the frictional function representing the interfacial forces working on the solute molecule from the membrane pore wall involved in the above model were initially determined by a trial-and-error method whereupon the solutions in terms of solute separation and the ratio of product rate to pure water permeation rate fit the experimental data. Subsequently, the potential function has been generated by using experimental data from high performance liquid chromatography (HPLC) in which the retention time represents the adsorption–desorption equilibrium of the solute at the solvent–polymer interface, while the frictional force has been expressed by a function of the ratio of a distance associated with steric repulsion at the interface to the pore radius (*32*). This approach has been extended to a variety of polymeric materials (*33*), and the use of liquid chromatography for studying interfacial properties relevant to reverse osmosis and ultrafiltration has been described (*34, 35*). More recently, the surface force parameters obtained from liquid chromatography data have been related to the structure of the solute molecule and to the repeating unit of the polymeric material (*36*). The force constants so obtained, together with the average pore size and its distribution, enable one to calculate solute separation and product rate for a membrane, and it is emphasized that the approach offers a guideline to the choice of membrane material as well as the pore size and pore size distribution, and thus is relevant to membrane design for specific applications.

## CONCLUSIONS

It is obvious from the above discussion that the mechanism of reverse osmosis transport is a subject of debate. Various approaches found in the literature show some similarities and dissimilarities among themselves. There is at least one thing in common: most of the theories describe the basic diffusive nature of the passage through the membrane. At one extreme, as in the solution–diffusion model, there is no clear-cut route to this passage, while others, like the preferential sorption–capillary flow mechanism, invoke definite pores and capillaries, and hence various troubles are encountered in the journey of the components.

The solution–diffusion model, and others like it, try to seek an alternative in the so-called homogeneous or perfect membranes which don't exist in practice. These mechanisms attempt to show that membranes which are apparently free from imperfections can give "theoretical" salt rejections. Maximum possible solute separation of 100% is also postulated by the preferential sorption–capillary flow mechanism when $P > \Pi_F$, but it seems difficult for the solution–diffusion model to explain lower separations, even with perfect membranes, when the operating pressure $P$ is less than the osmotic pressure $\Pi_F$ of the feed solution. The former has the ability to specify any membrane and a system, and to predict their performances with a minimum number of experimental data, while the others are limited and do not involve the fundamental parameters such as the pure water permeability constant, mass transfer coefficient and the solute transport parameter. The parameters $A$ and $B$ defined by the solution–diffusion model are somewhat similar to the pure water permeability constant and the solute transport parameter, respectively, given by the preferential sorption–capillary flow mechanism, but these are limited to particular experimental conditions. There are other limitations to most of the theories, as mentioned in the discussion, whereas the preferential sorption–capillary flow mechanism has received some support from other approaches. In this respect, the latter occupies a unique position, and it is possibly the most useful approach from a practical point of view. This theory does not, however, describe the nature of the flow through the membrane adequately. It assumes that the solute transport is due to pore diffusion through the capillaries, but it may not ignore the other types of flow, e.g., Poiseuille's flow or a composite of Poiseuille's flow and diffusive flow. The decision between the type of flow may be critical, especially if the pores are not uniform.

## Acknowledgments

This article is dedicated to Dr S. Sourirajan on the occasion of his 60th birthday. I am indebted to him for the inspiration during my graduate studies at the University of Ottawa which led me to the field of membrane research. I am particularly grateful to him, as well as to Dr T. Matsuura, for the stimulating freedom provided for learning during our collaboration at the National Research Council of Canada. The kind assistance of Dr K. H. Chan, another of my former colleagues, in typing the manuscript is also sincerely acknowledged.

## REFERENCES

*1.* S. Sourirajan, *Ind. Eng. Chem., Fundam.*, *2*, 51 (1963).
*2.* M. Soltanieh and W. N. Gill, *Chem. Eng. Commun.*, *12*, 279 (1981).
*3.* S. Kimura and S. Sourirajan, *AIChE J.*, *13*, 497 (1967).
*4.* S. Sourirajan, *Pure Appl. Chem.*, *50*, 593 (1978).
*5.* C. E. Reid and E. J. Breton, *J. Appl. Polym. Sci.*, *1*, 133 (1959).
*6.* H. K. Lonsdale, U. Merten, and R. L. Riley, *Ibid.*, *9*, 1341 (1965).
*7.* R. L. Riley, H. K. Lonsdale, C. R. Lyons, and U. Merten, *Ibid.*, *11*, 2143 (1967).
*8.* H. K. Lonsdale, B. P. Cross, F. M. Graber, and C. E. Milstead, *J. Macromol. Sci.—Phys.*, *B5*, 167 (1971).
*9.* A. S. Michaelis, H. J. Bixler, and R. M. Hodges, Jr., *J. Colloid Sci.*, *20*, 1034 (1965).
*10.* W. Banks and A. Sharples, *J. Appl. Chem.*, *16*, 153 (1966).
*11.* T. K. Sherwood, P. L. T. Brian, and R. E. Fisher, *Ind. Eng. Chem., Fundam.*, *6*, 2 (1967).
*12.* O. Kedem and A. Katchalski, *Biochim. Biophys. Acta*, *27*, 229 (1958).
*13.* K. S. Spiegler and O. Kedem, *Desalination*, *1*, 311 (1966).
*14.* J. Jagur-Grodzinski and O. Kedem, *Ibid.*, *1*, 327 (1966).
*15.* L. F. del Castillo, *Ibid.*, *19*, 211 (1976).
*16.* S. Sourirajan, *Ind. Eng. Chem., Process Des. Dev.*, *5*, 422 (1966).
*17.* T. S. Govindan and S. Sourirajan, *Ibid.*, *6*, 154 (1967).
*18.* S. Sourirajan and S. Kimura, *Ibid.*, *6*, 504 (1967).
*19.* T. S. Govindan and S. Sourirajan, *Ibid.*, *5*, 422 (1966).
*20.* R. Flores, A. Flores, and L. F. del Castillo, *Desalination*, *19*, 221 (1976).
*21.* E. Glueckauf, *Proceedings of the First International Symposium on Water Desalination*, Vol. 1, U.S. Department of the Interior, Washington, D.C., 1965, p. 143.
*22.* C. P. Bean, in *Membranes* (G. Eiseman, ed.), Dekker, New York, 1972, pp. 1–54.

23. Yu. N. Dytnerskii, G. V. Polyakov, and L. S. Lukavyi, *Theor. Found. Chem. Eng.*, *6*, 565 (1972).
24. W. R. Vieth, J. M. Howell, and J. H. Hsieh, *J. Membr. Sci.*, *1*, 177 (1976).
25. W. R. Vieth and A. S. Douglas, *J. Macromol. Sci.—Phys.*, *B3*, 737 (1969).
26. D. Woermann, *J. Membr. Sci.*, *7*, 127 (1980).
27. G. Jonsson, *Desalination*, *35*, 21 (1980).
28. B. V. Derjagin, N. V. Churaev, and G. A. Martynov, J. Colloid Interface Sci., *75*, 419 (1980).
29. P. Neogi and E. Ruckenstein, *Ibid.*, *79*, 159 (1981).
30. S. V. Fomichev and N. V. Kochergin, *Chem. Abstr.*, *94*, 163212 (1981).
31. T. Matsuura and S. Sourirajan, *Ind. Eng. Chem., Process Des. Dev.*, *20*, 273 (1981).
32. T. Matsuura, Y. Taketani, and S. Sourirajan, in *Synthetic Membranes*, Vol. II (A. F. Turbak, ed.), ACS Symposium Series 154, 1981, p. 315.
33. T. Matsuura, Y. Taketani, and S. Sourirajan, *Desalination*, *38*, 319 (1981).
34. Y. Taketani, T. Matsuura, and S. Sourirajan, *J. Electrochem. Soc.*, *129*, 1485 (1982).
35. Y. Taketani, T. Matsuura, and S. Sourirajan, *Sep. Sci. Technol.*, *17*, 821 (1982).
36. Y. Taketani, T. Matsuura, and S. Sourirajan, *Desalination*, *46*, 455 (1983).

*Received by editor December 9, 1983*