JOURNAL OF APPLIED POLYMER SCIENCE VOL. 11, PP. 1807–1820 (1967)

Phenol Transport in Cellulose Acetate Membranes

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Synopsis

Past detailed studies of solute transport through reverse-osmosis membranes have been conducted only with simple salts. The present work with phenol was undertaken largely because of the practical observation that the transport of low molecular weight organics is much more rapid than that of the salts. Studies of phenol sorption from dilute aqueous solution indicate that the diffusion coefficient for phenol in water-saturated 39.8 wt.-% acetyl cellulose acetate is 9.6×10^{-10} cm.^{2}/sec., and the equilibrium distribution coefficient between the acetate phase and water is 42. Thus, the diffusion coefficient is quite close to that measured for sodium chloride, and the higher permeability of the membranes to phenol can be attributed entirely to their greater sorption of this solute. In direct osmosis experiments performed with significant water flow a measurable interaction or positive coupling between water and phenol flows has been observed. Further evidence of flow coupling is derived from reverse osmosis experiments in which significant negative solute rejection is observed; i.e., the permeate is enriched in phenol by as much as 20%. It is shown that a solution-diffusion transport model is not adequate to rationalize the results, and a more complex transport model is apparently required.

INTRODUCTION

Since the discovery by Reid and Breton[1] that cellulose acetate can be used to prepare semipermeable membranes useful in the separation of water from aqueous solutions of sodium chloride and other salts there has been considerable interest in the mechanisms by which water and dissolved solutes are transported through such membranes. It now seems to be generally agreed[2,3] that water transport is best viewed as a simple solution-diffusion process, though, as has already been observed,[4] a real distinction between a solution-diffusion mechanism of water transport and other mechanisms (in particular viscous flow with solute filtration) cannot be made on the basis of transport measurements alone when the membrane is ideally semipermeable, as it very nearly is in the case of cellulose acetate and aqueous sodium chloride.

In past work in this laboratory the mechanism of sodium chloride transport has also been studied in some detail.[2] The conclusions reached were based on three types of experimental observations: immersion measurements, direct-osmosis measurements, and reverse-osmosis measurements. In the immersion measurements previously water-saturated

cellulose acetate samples were immersed in sodium chloride solutions, and the salt sorption was measured as a function of time. These measurements allowed the permeability of the membranes to sodium chloride to be determined under such conditions that there was negligible simultaneous water transport and that membrane imperfections made relatively little contribution to the observed values.

These immersion measurements yielded permeabilities to sodium chloride substantially lower than those observed in reverse-osmosis measurements (with water and salt flows in the same direction), a result which could be attributed either to significant coupling of water and salt transport or to the existence of membrane imperfections. High permeabilities were also observed in direct-osmosis measurements (with water and salt flows in opposite directions), showing that coupled flow through the membrane as a whole was not the principal reason for the discrepancies and that the existence of imperfections was the only plausible explanation.

In separate reverse-osmosis measurements Blunk[5] and Keilin[6] showed that cellulose acetate membranes, which are effective in separating water from solutions of simple salts, are not effective in separating small organic molecules, including a variety of alcohols and ketones, from water. This raises the question whether these non-ionized solutes also show uncoupled diffusion and behave differently from sodium chloride, simply because the membrane is more permeable to them in a solution-diffusion sense, or whether they are carried through the membrane by water in a coupled process. The present work was undertaken to answer this question. Phenol was chosen as the solute for study as a matter of convenience and because of its importance as a contaminant in industrial waste streams.

EXPERIMENTAL

Most of the membranes used in this work were made by casting an acetone solution of 39.8% acetyl cellulose acetate (Eastman Chemical Products, Inc., 398-3) on a polished plate and permitting the solvent to evaporate. These membranes will be referred to as "normal" membranes. The "modified" membrane, which was used in the reverse-osmosis experiment, was prepared by a method like that described by Loeb and Sourirajan.[7] Immersion experiments were carried out much as described in an earlier work,[2] except that the amount of phenol sorbed was calculated from measurements of the decline in solute concentration in the immersion solution rather than by direct measurement of the solute sorption in the membrane.

Direct-osmosis measurements were made in the apparatus previously described.[2] The membrane area was 260 cm.^{2}, and the two solution chambers, when filled, contained 2.83 liters (chamber I) and 2.75 liters (chamber II) of solution. In each experiment a solution of approximately 100 ppm phenol was placed in one chamber and a solution without phenol was placed in the other. To cause water to flow through the membrane

at significant rates, sucrose was added to one of the two solutions in some of the experiments. In one experiment equal concentrations of sucrose were placed in the two chambers, to measure the effect of decreased water activity on the permeability of the membrane to phenol. Phenol permeation was determined by analyzing both solutions at intervals for phenol, and water flow was measured by collecting overflow, in a buret, from the chamber with the concentrated sucrose solution. The solutions in both chambers were agitated with stirrers under conditions that have previously been found sufficient to avoid significant boundary layer effects.

To obtain reliable water flow data it was sometimes necessary to leave the experiment undisturbed for a time that was inconveniently long for the phenol measurements. Therefore, the phenol flows and water flows in those cases were measured in separate, but essentially identical, experiments.

All direct-osmosis measurements were carried out with two nominally identical normal membranes at 25.0 ± 0.1°C. Reagent grade phenol was used throughout.

The reverse-osmosis experiments were performed in an apparatus described previously[2] with the use of both normal and modified membranes. The high-pressure solution of approximately 70–80 ppm phenol was circulated over the surface of the membranes at high linear velocity (>200 cm./sec.), where boundary layer phenomena are known to be unimportant for these membranes.[8] Phenol and water permeation rates were determined as a function of the applied pressure by sampling both the high-pressure feed solution and the permeate and by measuring the rate of permeate flow. The reverse-osmosis experiments were performed at ≈30°C.

Phenol analyses were performed by a spectrophotometric method with 4-aminoantipyrine as color-developing agent.[9] The sucrose solutions were made from reagent-grade sucrose and laboratory distilled water. Sucrose analyses were performed on certain very dilute solutions by a spectrophotometric method based on the use of anthrone as color-developing agent.[10]

RESULTS

Immersion Experiments

The diffusion coefficient of phenol was obtained in the immersion experiments by applying the solution to the problem of "diffusion from a stirred solution of limited volume," as described by Crank.[11] The phenol solution, in which pieces of membrane of known thickness were immersed, was periodically sampled and analyzed. The volume of sample required for analysis was trivial relative to the volume of the immersion solution, but the amount of phenol sorbed by the membrane was a significant fraction of the total phenol present. The solution to Fick's law with the

appropriate boundary conditions is graphically presented by Crank[11] in the form of a plot of M_t/M_∞ versus $(Dt/L^2)^{1/2}$ for several values of the percentage of total solute finally taken up by the membrane. In the plotted equations L is the half-thickness of the membrane, M_t is the total amount of solute in the membrane at time t, and M_∞ is the corresponding quantity at equilibrium. The amount sorbed was calculated from the decreasing phenol concentration in the immersion solution and by assuming that the missing phenol was sorbed by the membrane. To calculate the diffusion coefficient, Crank's values for relative amount sorbed versus reduced time

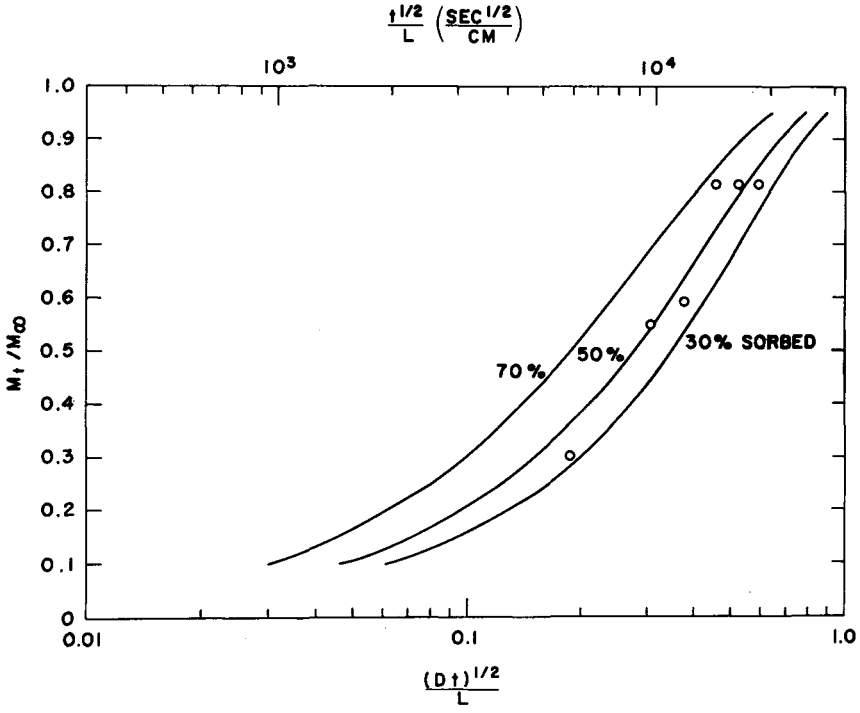

Fig. 1. Phenol sorption in immersion experiment.

were replotted in the form of M_t/M_∞ versus log $(Dt/L^2)^{1/2}$, and the observed values were plotted as M_t/M_∞ versus log $(t/L^2)^{1/2}$. In this manner D was obtained by superimposing one plot on the other and by noting the transposition of axes necessary to make the experimental points coincide with the proper member of the theoretical family of curves. The results of this procedure are presented in Figure 1. In the present case the membrane sample was 23 $\pm$ 1 μ thick and weighed 6.61 g. The sample was immersed in 283 ml. of water that initially contained 96.5 ppm phenol; 48% of the phenol initially present in the solution was taken up by the membrane. The value of D obtained by this procedure is 9.6×10^{-10} cm.^{2}/sec.

TABLE I
Summary of Direct-Osmosis Experiments at 25°C.

Membrane no.	Expt. no.	Sucrose concn., molal	Water flow, 10^{-2} cm.^{3}/min.	Water perm. D_1c_1, 10^{-7} g./cm.-sec.	Direction of water flow relative to phenol flow	Phenol perm. D_2K_2, 10^{-8} cm.^{2}/sec.
1	A	0	Not detectable	—	None	3.77
1	B	0.50	Not determined	—	Opp.	3.48
1	C	0.50	Not determined	—	Same	3.58
2	D	3.21	5.1	1.6	Opp.	2.58[a]
2	E	3.21	6.1	1.9	Same	2.96[a]
2	F	3.21	6.0	1.9	Same	3.67
2	G	3.21	6.0	1.9	Opp.	2.68
2	H	1.80, 1.80[b]	Not detectable	—	None	3.22
2	I	3.21	6.1	1.9	Same	3.49

[a] These data have been discarded.
[b] Equal sucrose concentrations in the two chambers.

Three additional, similar immersions were measured to obtain a good value for the distribution coefficient at equilibrium. In all cases the immersion lasted 4 hr. or more. The mean value for the distribution coefficient K, expressed as grams of phenol per cubic centimeter of cellulose acetate divided by grams of phenol per cubic centimeter of solution, was found to be 41.9 with a standard deviation of ± 2.9. The density of cellulose acetate when saturated with water was taken as 1.25 g./cm.^{3} to give this value.

Direct-Osmosis Experiments

Some preliminary direct-osmosis measurements were performed in which only the water and sucrose flows were measured. When there was no sucrose in either solution, the water flow was too small to permit measurement. In an experiment in which the solution initially containing 100 ppm phenol was 0.50 molal in sucrose, the concentrated-solution volume increased steadily at an average rate of 9.2×10^{-3} cm.^{3}/min. during a 4-day period. The membrane was $40 \pm 2\mu$ thick. In another experiment with the same membrane, in which the initially phenol-free solution was 0.50 molal in sucrose, the volume of the concentrated sucrose solution increased steadily at an average rate of 10.3×10^{-3} cm.^{3}/min. during a 3-day period.

Analyses were made for sucrose in the chamber initially containing none at the end of some of the preliminary experiments. The results were negative. In the case in which the lowest analytical limits can be set the sucrose transport was less than 2.5×10^{-4} g. in 119 hr.

In addition to these preliminary studies a total of nine direct-osmosis experiments were performed. The experimental conditions and the results are summarized in Table I. Experiments A through C were performed with the same membrane having a thickness of $37 \pm 2\ \mu$. Experiments D through I were performed with a separate, but nominally identical, membrane of the same thickness. In experiments B, D, and G the phenol and sucrose were in the same chamber in the osmosis cell, so that the flows of phenol and water were in opposite directions. In experiments C, E, F, and I the phenol and sucrose were in different chambers, and the flows of water and phenol were in the same direction. In experiment H both chambers were 1.80 molal in sucrose, and the flow of water was too small to detect. The osmotic pressures of sucrose solutions are given by Glasstone[12] at 30°C.; after correction to 25°C. the values are 12.7 atm. (0.50 molal), 51 atm. (1.80 molal), and 102 atm. (3.21 molal).

The water permeabilities presented in Table I were calculated from the water flow data by assuming a solution-diffusion model of water transport. It has been shown previously[2] that the flow of water through cellulose acetate membranes of the kind used here can be described by the equation

$$J_1 = -(D_1 c_1 \bar{v}_1 / RT\Delta x)(\Delta P - \Delta\pi) \qquad (1)$$

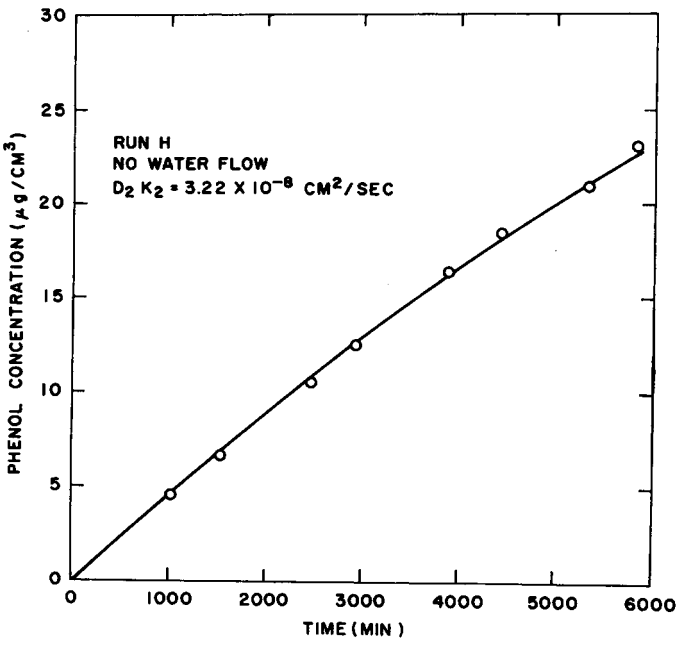

Fig. 2. Concentration of phenol versus time in direct-osmosis experiment.

where J_1 = mass flow of water per unit membrane area, D_1 = diffusion coefficient for water in the membrane, c_1 = concentration of water in the membrane, $\bar{v}_1$ = partial molar volume of water in the membrane, Δx = thickness of membrane, R = gas constant, T = absolute temperature, ΔP = pressure difference across membrane, and $\Delta\pi$ = osmotic pressure difference across membrane. In the present direct osmosis experiments $\Delta P = 0$.

In the preliminary measurements the water permeability (D_1c_1) values of 2.5×10^{-7} and 2.8×10^{-7} g./cm.-sec. were obtained for the case with phenol and 0.50 molal sucrose on the same side and on the opposite side of the membrane, respectively. These permeability values are both in good agreement with the value 2.6×10^{-7} g./cm.-sec. reported earlier,[2] but the remaining data in Table I indicate that the water permeability of cellulose acetate decreases somewhat with increasing osmotic pressure of the external solution.

The permeability of the membranes to phenol was determined by sampling both chambers of the osmosis cell periodically to determine the transport rate. Actually, only the concentration in one chamber was required, the other analyses being made only to check whether good analytical closures were obtained. In the worst case the sum of the two analyses differed from the expected result by 4%, and generally the closure was within 2%. A typical plot of phenol concentration in the initially phenol-free chamber as a function of time is presented in Figure 2.

The analysis of the phenol flow results can be made in terms similar to those used earlier for sodium chloride.[2] Thus, we write

$$J_2 = -D_2(dc_2/dx) \tag{2}$$

where J_2 = mass flow of phenol per unit membrane area, D_2 = diffusion coefficient for phenol in the membrane, c_2 = concentration of phenol in the membrane, and x = distance measured perpendicular to the membrane surface.

We shall assume that the phenol concentration at the membrane surface is always in chemical equilibrium with that in the surrounding solution and that, therefore, at the surface

$$c_2 = K_2\rho_2 \tag{3}$$

where ρ_2 is the phenol concentration in the external solution, and K_2 is the distribution coefficient for phenol between its aqueous solution and 39.8 wt.-% acetyl cellulose acetate.

Assuming that D_2 and K_2 are independent of ρ_2 and integrating eq. (2), we obtain

$$J_2 = -D_2K_2(\Delta\rho_2/\Delta x) \tag{4}$$

The concentration change in the chamber initially containing no phenol is, then,

$$d\rho_2''/dt = D_2KA/V''\Delta x(\rho_2' - \rho_2'') \equiv (B/V'')(\rho_2' - \rho_2'') \tag{5}$$

where the single and double primes refer to the chamber initially containing phenol and that containing no phenol, respectively, A is the membrane area, and V is the volume of one chamber. Equation (5) applies only after the initial approach to steady state but, compared to this transient, the times of interest here are long.

Approximate values for the constant B are readily obtained from eq. (5) when the effects of sampling and water transport are neglected. Phenol conservation then requires

$$V'\rho_2' + V''\rho_2'' = V'\rho_{20}' \tag{6}$$

where ρ_{20}' is the initial phenol concentration in the indicated chamber. When eq. (5) is integrated,

$$1 - (\rho_2''/\rho_{20}')[(V' + V'')/V'] = \exp\{-[(V' + V'')/V'V'']Bt\} \tag{7}$$

where t is time measured from the beginning of the experiment.

More accurate determination of B in the present case is possible if explicit account is taken of the phenol and water losses that occur owing to sampling and the water that is transported owing to the osmotic pressure difference. Since the sample volumes withdrawn at each sampling time are known, it is possible to compute complete curves of ρ_2'' versus t for assumed values of B by the following procedure. Equation (7) is used to calculate ρ_2' and ρ_2'' at the first sampling time. Then V', V'', and the

total phenol inventory are adjusted as required by the sample volumes removed and these calculated concentrations. Next, the procedure is repeated with the new boundary conditions in an equation like eq. (7), to calculate concentrations at the second sampling time, and so on. The effect of water transport through the membrane (a relatively small effect on the volumes) is included by taking the observed water flow and adding it to, or subtracting it from, the sample volumes removed at the end of each interval, as appropriate. In experiments B and C the water flow was not observed directly, and the water permeabilities obtained in the preliminary measurements were used along with eq. (1) to calculate the anticipated amount of water flow in each interval.

This procedure was used in a computer program to calculate the complete curve of concentration versus time for each experiment. The optimum value of B was obtained by a least-squares-fit analysis, and the permeability to phenol, D_2K_2, was calculated from B and the membrane thickness and area as

$$D_2K_2 \equiv B\Delta x/A \tag{8}$$

The results of two experiments were discarded. In experiment D the plot of concentration versus time was highly scattered, and the good agreement with repeat experiment G is considered fortuitous. Experiment E was not of poor analytical quality, but it deviated markedly from the two repeat experiments F and I.

The remaining phenol permeability data are plotted in Figure 3 against the mean water activity in the two chambers of the osmosis cell. For comparison, the "immersion" value of the phenol permeability, $D_2K_2 = 4.0 \times 10^{-8}$ cm.^{2}/sec., is presented in the same plot.

Reverse-Osmosis Experiments

Reverse-osmosis experiments were performed with both normal and modified membranes. Normal membranes were used for consistency, because the other transport measurements were made with these membranes. However, the water flows observed in reverse osmosis (0.0016–0.0054 cm.^{3}/min. at pressures of 34–102 atm.) were so small that the product water samples, even after many hours, were inadequate to permit precise analysis. Modified membranes were used because they permit higher water flows (0.46–1.2 cm.^{3}/min.) under the same conditions. The more reliable reverse-osmosis data were obtained with modified membranes, and the normal membranes were tested in the same system, to ensure that the two types of membrane exhibit qualitatively the same relative permeability to water and phenol.

The reverse-osmosis results are expressed in terms of "solute rejection." defined as

$$\text{solute rejection} \equiv (\rho_2' - \rho_2'')/\rho_2' \tag{9}$$

where the single and double primes refer to the high-pressure solution and the permeate, respectively. All experiments were performed on two or more nominally identical membranes.

The results at three different operating pressures are presented in Table II. The experiments with the modified membranes were reproducible, and

TABLE II
Reverse-Osmosis Results at ≈30°C.

Applied pressure, atm.	Membrane	Solute rejection, %
34	Modified	−10.8, −10.8
68	Modified	−17.4. −20.2
68	Normal	−10.4, +1.3
102	Modified	−20.3, −22.9
102	Normal	−27.1, −16.9, −13.9, −10.7, −25.7

significant negative rejection (i.e., permeate enrichment) was observed in each case. The experiments with the normal membranes exhibited significantly greater scatter but were otherwise qualitatively in agreement with the modified-membrane experiments.

The water permeability of the normal membranes, calculated from the water flux and eq. (1) with $\Delta\pi = 0$, was in the range 1.9×10^{-7} to 2.4×10^{-7} g./cm.-sec., which is in acceptable agreement with the direct-osmosis measurements and with previous measurements of the water permeability of 39.8% acetyl cellulose acetate.

DISCUSSION

It is immediately obvious that the permeability of these cellulose acetate membranes to phenol is exceedingly high. The permeability coefficient of 4×10^{-8} cm.²/sec. is to be compared with the value of about 3×10^{-11} cm.²/sec. for sodium chloride[2] and even smaller values for salts of several divalent ions.[13] The higher permeability is attributable to a greater solubility of phenol in the membrane material. The distribution coefficient for phenol is 42, whereas that for sodium chloride is only 0.03; the diffusion coefficients for these two species in cellulose acetate are very nearly equal.

The large distribution coefficient is probably responsible for the unusual findings in the work of both Blunk[5] and Keilin[6] that the water flow through their modified membranes was sharply reduced in the presence of phenol. If the distribution coefficient for phenol is assumed concentration-independent, one can show that the membranes used in their experiments were highly concentrated in phenol in the presence of moderate external solution concentrations, 5.25 wt.-% in Blunk's research and 1.0 wt.-% in the studies of Keilin. It is not surprising that the water permeability of this new

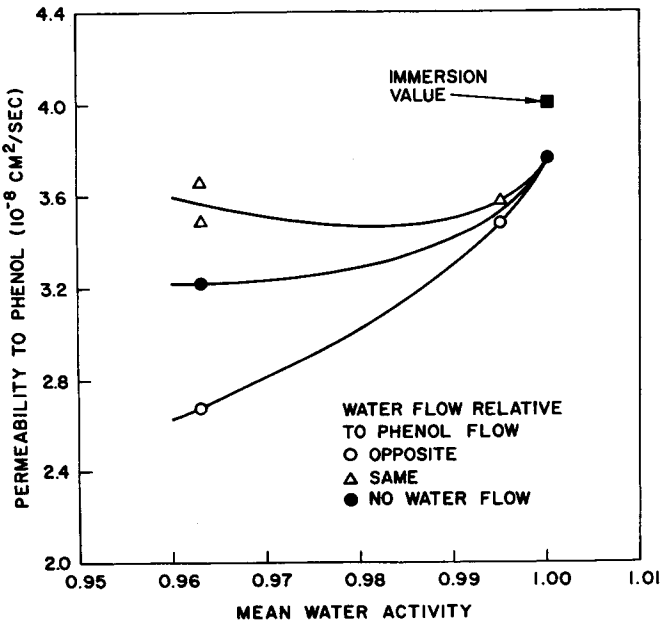

Fig. 3. Permeability to phenol versus mean water activity in direct-osmosis experiment.

membrane material, phenol–cellulose acetate, is markedly lower than that of pure cellulose acetate, a material noted for its exceptionally high permeability to water. At the concentrations used in the present experiments (100 ppm external, and $\approx 0.4\%$ internal, concentration) this effect was not apparent.

The permeability of the membranes to phenol is dependent on both the water activity in the external phase and on the direction and magnitude of water flux (Table I and Fig. 3). That the two flows interact cannot be attributed to the presence of membrane imperfections (the effect of which would be small in the present experiments, because the membranes are highly permeable to phenol), but must be a manifestation of flow coupling.

The solution-diffusion model of membrane transport cannot be used to account for the dependence of phenol flux on water flux, nor can the high negative phenol rejections in reverse osmosis be accounted for in this way. In the uncoupled solution-diffusion model[4] the solute flow is given by

$$J_2 = -(D_2c_2/RT)[(\partial\mu_2/\partial c_2)_{P,T}(dc_2/dx) + \bar{v}_2(dP/dx)] \qquad (10)$$

where μ_2 is the chemical potential of solute and $\bar{v}_2$ is its partial molar volume; the other terms have been defined. It is customary to neglect the second term when the membrane is highly semipermeable and the molar volume of the solute is small. Neither of these criteria is met in the present case, and the second term represents a significant contribution to the driving force for solute.

If we make the assumption that activity is proportional to concentration, which is valid in dilute solutions, then

$$(\partial\mu_2/\partial c_2)_{P,T} = RT/c_2 \tag{11}$$

and eq. (10) becomes on integration, as follows:

$$J_2 = -D_2K_2(\Delta\rho_2/\Delta x) - D_2K_2\rho_2(\bar{v}_2/RT)(\Delta P/\Delta x) \tag{12}$$

Recognizing the fact that the solute concentration in the permeate in reverse osmosis is determined by the relative flows of solute and solvent, we have

$$\rho_2'/\rho_2'' = \rho_2'J_1/\rho_1''J_2 \tag{13}$$

where ρ_1 is the concentration of water in the aqueous phase. When one substitutes from eqs. (1) and (12) into eq. (13),

$$\rho_2'/\rho_2'' = (\rho_2'/\rho_1'')[D_1c_1\bar{v}_1\Delta P/(D_2K_2RT\Delta\rho_2 + D_2K_2\rho_2'\bar{v}_2\Delta P)] \tag{14}$$

when $\Delta\pi = 0$. (It makes little difference in the final result whether we use ρ_2' or ρ_2'' in the second term in the denominator. The correct choice depends on the response of the membrane to the applied pressure.) If we define K_1 as the distribution coefficient for water, i.e., $K_1 \equiv c_1/\rho_1 \approx c_1$, then eq. (14) becomes

$$\rho_2'/\rho_2'' = D_1\bar{v}_1K_1\Delta P/[D_2K_2RT(\Delta\rho_2/\rho_2') + D_2K_2\bar{v}_2\Delta P] \tag{15}$$

and, solving for ρ_2'/ρ_2'', we obtain

$$\rho_2'/\rho_2'' = (D_1\bar{v}_1K_1\Delta P + D_2K_2RT)/[D_2K_2(RT + \bar{v}_2\Delta P)] \tag{16}$$

The solute rejection, defined by eq. (9), can then be calculated from the permeability of the membrane to water and to phenol, the partial molar volumes, and the applied pressure.

The partial molar volume of phenol can be estimated either from data on the density of aqueous phenol solutions[14] or from the bulk density and molecular weight. The values are 92 and 88 cm.^{3}/mole, respectively, and for this calculation $\bar{v}_2$ is taken as 90 cm.^{3}/mole. Using the mean observed water permeability in reverse osmosis of 2.1×10^{-7} g./cm.-sec. and a mean observed phenol permeability at 25°C. of 3.9×10^{-8} cm.^{2}/sec., one can calculate phenol rejections of approximately -1, -2, and -3%, respectively, at the three operating pressures given in Table II. (An activation energy for phenol permeability of 7 kcal./mole has been used to adjust the 25°C. value to 30°C.) Clearly, these values are all considerably smaller than the observed rejections. If one were to neglect the $\bar{v}_2dP$ term in eq. (10), the calculated rejections would all be small and positive, increasing the discrepancy.

In conclusion, all the evidence points to significant coupling of water and phenol flows and an inadequacy of the solution-diffusion flow model in this case. The use of a coupled flow model and a satisfactory rationaliza-

tion of the immersion, the direct-osmosis, and the reverse-osmosis data will be discussed elsewhere.[15]

From the practical point of view it is noteworthy that these cellulose acetate membranes cannot be used to remove phenol from water in a conventional reverse-osmosis device. The product water is enriched in phenol at all concentrations, and the effect becomes greater with increasing pressure.

This work was supported by the Office of Saline Water, U. S. Department of the Interior.

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Résumé

Les études détaillées antérieures concernant le transport de solutés à travers des membranes par osmose inverse ont été effectuées uniquement sur de simples sels. Dans le présent travail consacré au transport du phénol, on s'est basé sur l'observation pratique que le transport de produits organiques de bas poids moléculaire est beaucoup plus rapide que celui des sels. Des études de la sorption du phénol au départ de solutions aqueuses diluées indiquent que le coefficient de diffusion pour le phénol dans l'acétate d'acétyle cellulose saturé en eau (39.8% en poids) est de 9.6×10^{-10} cm²/sec, et que le coefficient de distribution à l'équilibre entre la phase acétate et l'eau est de 42. Donc le coefficient de diffusion est très voisin de celui qu'on mesure pour le chlorure de sodium

et la perméabilité plus élevées des membranes vis à vis du phenol peut être attribuée entièrement à la sorption plus élevée de ce soluté. Dans les expériences d'osmose directe effectuées avec un écoulement d'eau important, une interaction mesurable ou un couplage positif entre les écoulements d'eau et de phénol à été observé. Le couplage à l'écoulement a été mis en évidence au moyen d'expériences d'osmose inverse dans lesquelles un rejet négatif important du soluté a été observé, c'est-à-dire que la substance subit un enrichissement en phénol de 20%. On montre que le modèle de transport par diffusion dans la solution n'est pas adéquat pour rendre compte des résultats, et un modèle de transport plus complexe semble nécessaire.

Zusammenfassung

Frühere Versuche über den Transport gelöster Stoffe durch Membrane mit umgekehrter Osmose wurden nur mit einfachen Salzen ausgeführt. Die vorliegende Arbeit mit Phenol wurde zum grossen Teil deshalb unternommen, weil experimentell beobachtet wurde, dass der Transport niedermolekularer organischer Stoffe sehr viel rascher verläuft als derjenige von Salzen. Die Untersuchung der Phenolsorption aus verdünnter wässriger Lösung zeigt, dass der Diffusionskoeffizient von Phenol in wassergesättigtem Celluloseacetat mit 39,8 Gew.% Acetyl $9{,}6 \times 10^{-10}$ cm²/sec beträgt und der Gleichgewichtsverteilungskoeffizient zwischen Acetatphase und Wasser 42 ist. Somit liegt der Diffusionskoeffizient ganz nahe bei dem an Natriumchlorid gemessenen und die höhere Permeabilität der Membranen für Phenol kann zur Gänze auf ihre grössere Sorption dieses gelösten Stoffes zurückgeführt werden. Bei direkten mit einem wesentlichen Wasserfluss durchgeführten Osmoseversuchen wurde eine messbare Wechselwirkung oder positive Koppelung zwischen Wasser- und Phenolfluss beobachtet. Weitere Belege für eine Flusskoppelung werden aus Versuchen über umgekehrte Osmose abgeleitet, bei welchen eine wesentliche negative Abweisung des Gelösten beobachtet wird, d.h. das Permeat ist an Phenol zu bis zu 20% angereichert. Es wird gezeigt, dass ein Lösungs-Diffusionstransport-Modell keine adäquate Beschreibung der Ergebnisse erlaubt; offenbar ist ein mehr komplexes Transportmodell notwendig.

Received April 5, 1967
Prod. No. 1612