

## Pressure-Induced Diffusion of Organic Liquids Through Highly Swollen Polymer Membranes\*

D. R. PAUL and O. M. EBRA-LIMA, *Department of Chemical Engineering, The University of Texas, Austin, Texas 78712*

### Synopsis

The transport of twelve organic liquids through a highly swollen rubbery membrane has been studied. The transport was caused by a pressure applied to the liquid above the membrane (reverse osmosis). The flux was found to be a highly nonlinear function of the driving pressure. Detailed thermodynamic and diffusion theories are proposed to describe the transport in terms of the concentration gradient of the swelling liquid within the membrane induced by the applied pressure. The data and the theory appear to be in very good agreement. The diffusion coefficients deduced from the data are explained in terms of a hydrodynamic mechanism of diffusion. Highly swollen membranes can yield very high liquid fluxes at moderate pressure and consequently may have applications for performing certain separations.

### INTRODUCTION

The transport of gases, vapors, and liquids through polymeric membranes has received a great deal of attention as attested by recent reviews.<sup>1-3</sup> Interest stems in part from practical concerns about the barrier properties and chemical resistance of important polymers and the possibility of separating mixtures of compounds by membrane diffusion or permeation.<sup>4-10</sup> Transport caused by applying a pressure differential across the membrane is a particularly interesting method of effecting certain types of separations. This mode of operation is referred to as reverse osmosis when the mechanism of transport is molecular diffusion of penetrant molecules dissolved in the membrane, and as ultrafiltration when it is viscous flow through pores in the membrane. Over the past several years a great deal of research has been devoted to purifying water, in particular desalination, by reverse osmosis. Purification of materials of biological interest by ultrafiltration has also received considerable attention.

Most research on hydrostatic pressure-driven membrane separation processes has dealt with aqueous systems and has utilized hydrophilic polymers, e.g., cellulose acetate, as the membrane material. It is reasonable to expect that such methods should have many applications to organic

\* Presented at the Symposium on Tailored Polymeric Materials for Advanced Separation Processes, A.I.Ch.E. 62nd Annual Meeting, Washington, D.C., 1969.

fluids provided suitable membranes are used. Some work has already been reported where organic mixtures have been separated using the same type of membranes that are useful for aqueous systems.<sup>11,12</sup> It thus seems appropriate to look at the pressure-induced transport of organic liquids through membranes prepared from various types of polymers.

The work reported here is a preliminary study on transport of organic liquids through a crosslinked polymer which is highly swollen by the penetrating liquid. Such a system is interesting and novel for a number of reasons. First, it offers a relatively simple model system for fundamental studies on pressure-induced membrane transport. Second, it should be possible to develop very high penetrant fluxes because of the high diffusion coefficients and concentration gradients that are possible owing to the high degree of swelling. No actual separations have been performed yet with such systems; however, future work in this area is planned. The selectivity of such a membrane for similar molecules is not expected to be great because of the high degree of swelling; however, application to separations where there is a large difference in molecular size or thermodynamic nature of the components may be attractive.

Results on just one polymer are reported. This material was a cross-linked pure gum rubber sheeting (0.0265 cm thick) obtained from W. H. Curtin and Co.

### PERMEATION MEASUREMENTS

The experimental procedure followed closely the techniques often employed in desalination by reverse osmosis.<sup>9</sup> A high-pressure test cell supplied by the Amicon Corporation (Model 420) was employed for the flux measurements after some modifications. Figure 1 illustrates schematically the essential features of this apparatus. The membrane rests on a stainless steel porous plate. The liquid in the region above the membrane is pressurized while that below it remains at atmospheric pressure.

The membranes used were highly swollen by the liquids to be transported. In many cases the membrane contained at equilibrium four times as much solvent as polymer on a volume basis. The membranes were installed in the test cell in this highly swollen state by preswelling them to equilibrium and then maintaining a liquid environment about the cell during assembly. This procedure requires considerable technique to accomplish properly when very volatile liquids are used. Flow around the membrane is prevented by an O-ring that contacts its periphery. The force required to make this seal is generated by tightening the threads which attach the lower portion of the cell. After assembly, it was imperative to displace all air from the downstream compartment by filling it with liquid. To do this, the assembled cell was inverted and liquid was injected through a hole bored in the bottom of the cell specifically for this purpose. This position allowed the air to be displaced. Once properly filled, this hole was sealed off.

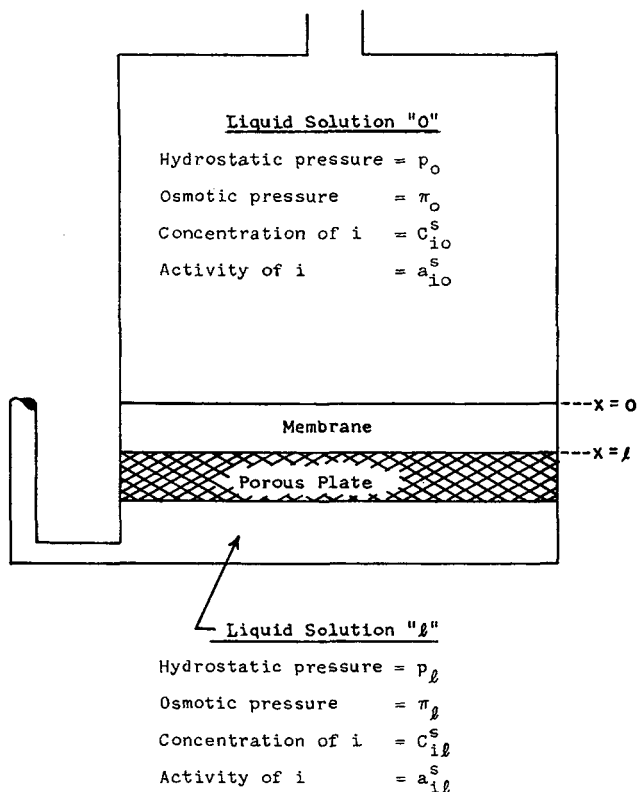


Fig. 1. Schematic illustration of apparatus used for flux measurements.

The fluxes were sufficiently small to necessitate special procedures to insure accurate measurements. This was done simply by connecting a vertical length of small-bore glass tubing to the downstream side of the cell by means of flexible tubing. The flow through the membrane could then be accurately determined from the rate of rise of the liquid meniscus up the glass tube, provided all air had been displaced from the downstream compartment of the cell. Erratic readings and the ultimate appearance of air bubbles in the measuring tube were very apparent when all of the air had not been displaced. The Amicon cell was not designed to be used in this way, since any slight positive head inside the downstream compartment caused leakage of liquid up through the mechanical threads which attach this portion of the cell. It was necessary to stop this leakage to use the vertical glass tube scheme. This was accomplished by machining off the last  $\frac{1}{4}$  in. of threads (both male and female) on the lower portion of the cell and installing an O-ring to seal in a slip fashion.

The upstream side of the cell was completely filled with the liquid and then connected by stainless steel tubing to the bottom of a reservoir also filled with liquid. A nitrogen pressure was applied above the liquid in the

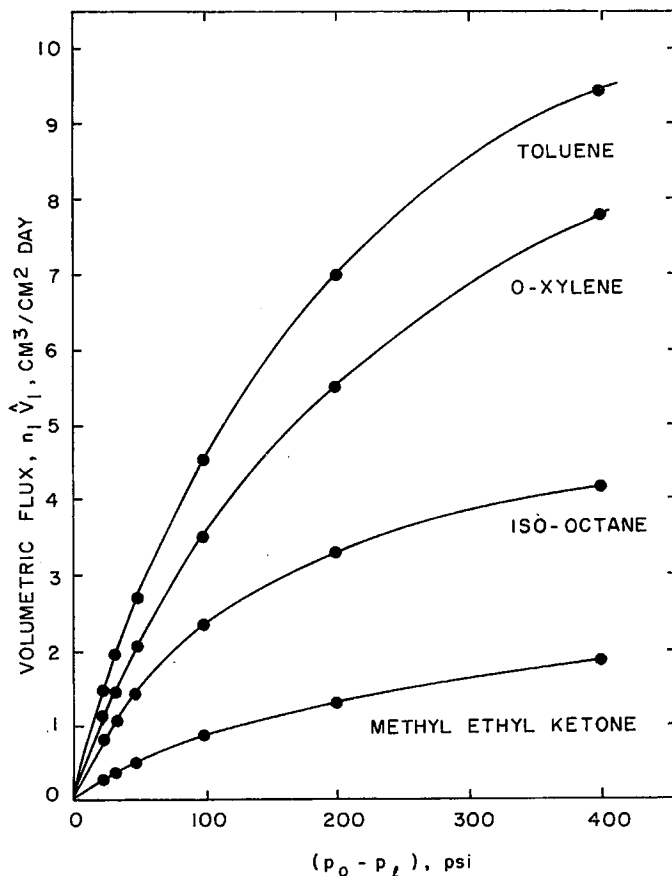


Fig. 2. Flux-pressure relationship.

reservoir to pressurize the upstream side of the membrane. The pressure was measured to the nearest psi on one of three test gauges depending on the range of the pressure. No circulation of the upstream liquid was necessary since only pure components were employed.

The entire test cell and the measuring capillary were immersed in a water bath set at  $30^\circ\text{C}$ . After applying a certain pressure to the upstream side, enough time was allowed for a steady permeation rate to be established. Normally 15 min proved adequate. The time required for the meniscus to move past fixed marks on the capillary was noted. From this observation the flow rate was determined. At least three duplicate observations were made at each condition. Reproducibility was excellent. The flux was determined by dividing the total flow rate by the active membrane area ( $36.7 \text{ cm}^2$ ) defined by the O-ring. The membrane has a tendency to shrink in area on the downstream side once it is pressurized; however, the O-ring prevents this.

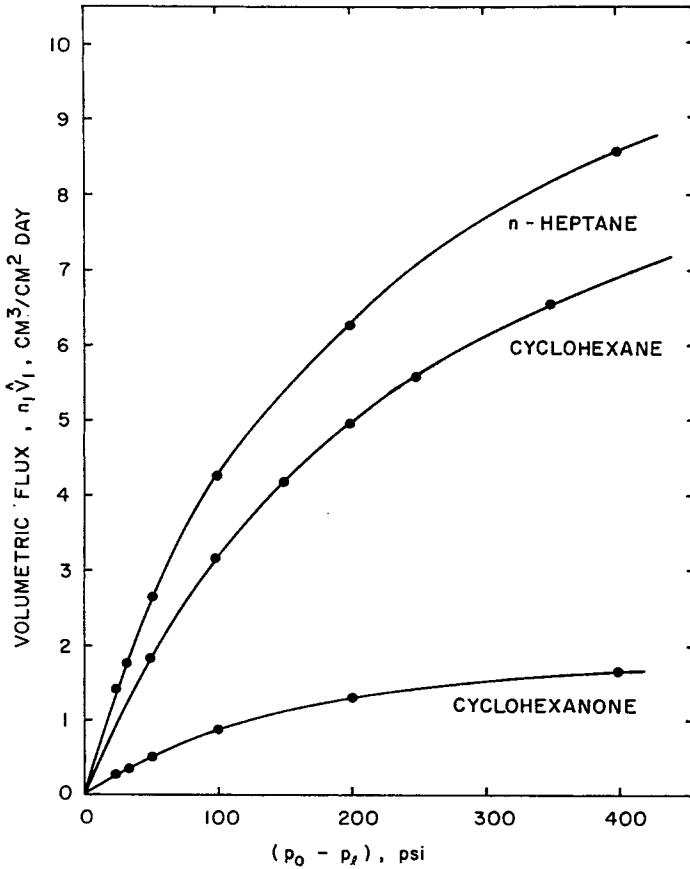


Fig. 3. Flux-pressure relationship.

Experimental results for twelve different organic liquids and a single crosslinked pure gum rubber membrane are reported here. These results are shown in Figures 2-4. The pressure range covered for nearly all compounds is 25 to 400 psi. The fluxes are expressed volumetrically in the units of  $\text{cm}^3/\text{cm}^2 \cdot \text{day}$  and are denoted by the symbol  $n_1 \hat{V}_1$ . These units may be converted rapidly to those more often used in reverse osmosis by the following factor:  $1 \text{ gal}/\text{ft}^2 \cdot \text{day} = 4.07 \text{ cm}^3/\text{cm}^2 \cdot \text{day}$ . It is interesting to note that the relationship between flux and pressure, which is entirely reversible, is not at all linear here. Most desalination membranes show a linear relationship except for a loss due to compaction, which is irreversible for the most part.

In the following sections an explanation of these nonlinear relations will be given in terms of a combined thermodynamic and diffusion theory for pressure-induced transport. The approach will be to examine carefully the concentration gradient induced by the applied pressure and the attendant diffusion caused by it.

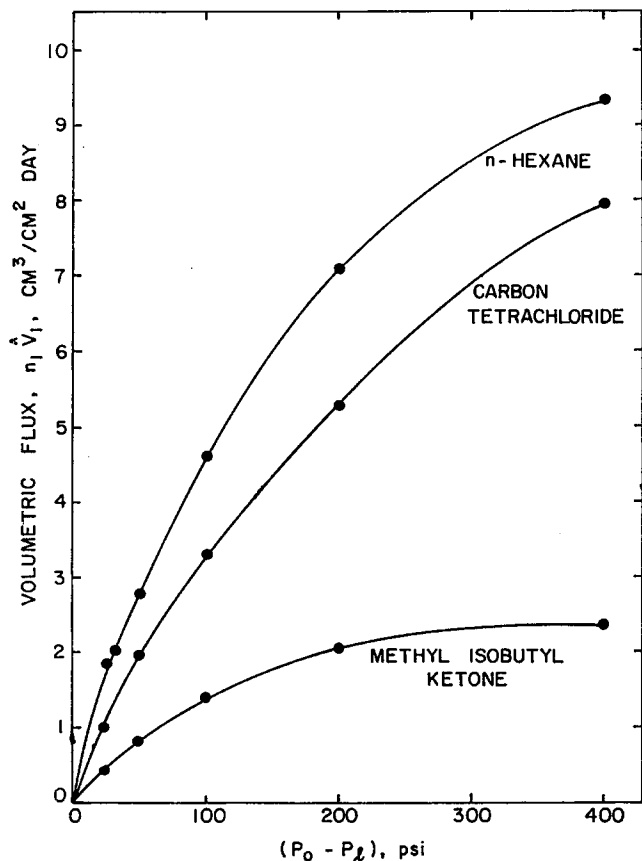


Fig. 4. Flux-pressure relationship.

### DEVELOPMENT OF A THERMODYNAMIC THEORY

To explain pressure-induced diffusive transport through a membrane, it is necessary to first show that this pressure difference leads to a concentration difference across the membrane and then develop a mathematical model by which this difference can be calculated since it is not usually possible to measure it directly.

The thermodynamic theory is developed by considering a rigid porous plate whose pores are intercommunicating. These pores may be arbitrarily small, but for practical reasons they should be large enough to permit easy flow of a low viscosity liquid. The polymer membrane of interest is placed over this porous plate, as shown in Figure 1. A liquid solution designated "0" contacts the top membrane surface ( $x = 0$ ), while a different solution "l" is below the porous plate but contacts the lower membrane surface ( $x = l$ ) through the intercommunicating pores of the rigid plate. Uniform but different hydrostatic pressures are maintained on the two solutions. Likewise, the activity and concentration of any component

$i$  are uniform within each solution but may not be equal. Concentrations and activities within the liquid solutions and the membrane are distinguished by the subscripts 0 and  $l$ . Thus,  $a_{i0}^m$  symbolizes the activity of component  $i$  at  $x = 0$  just within the membrane surface. Additional nomenclature is shown in Figure 1.

At constant temperature, the chemical potential of  $i$  in either solution or the membrane is a function of the pressure and the concentration of  $i$  at a particular point. For convenience, we chose to write the pressure dependence of the chemical potential explicitly so that the activity is primarily concentration dependent and pressure independent and completely so if  $\bar{V}_i = V_i$  as we will assume. Thus, for the two solutions we write

$$\mu_{i0}^s = \mu_i^0 + RT \ln a_{i0}^s + V_i(p_0 - p_r) \quad (1)$$

$$\mu_{il}^s = \mu_i^0 + RT \ln a_{il}^s + V_i(p_l - p_r) \quad (2)$$

where  $\mu_i^0$  refers to pure  $i$  at the arbitrary reference pressure  $p_r$ . The change in chemical potential for component  $i$  going from solution 0 to  $l$  is

$$\Delta\mu_i = \mu_{il}^s - \mu_{i0}^s = RT \ln \frac{a_{il}^s}{a_{i0}^s} - V_i(p_0 - p_l). \quad (3)$$

Substituting the definition of osmotic pressure,  $\pi$ , into eq. (3) gives

$$\Delta\mu_i = V_i[(\pi_0 - \pi_l) - (p_0 - p_l)], \quad (4)$$

which is the chemical potential driving force frequently used in phenomenological formulations of reverse osmosis.<sup>9</sup>

It is important to note that eq. (4) has been developed without any reference to the nature of the membrane or how species  $i$  interacts with it or what the pressure distribution within the membrane is. Such an approach is not adequate for a complete diffusion analysis of pressure-induced membrane transport. A more detailed model of what is occurring in the membrane is required for this. Specifically, the pressure distribution within the membrane is required. Rosenbaum and Cotton<sup>13,14</sup> have considered this problem and have enumerated three possible membrane pressure,  $p_m$ , distributions: (a)  $p_m = p_0$ , (b)  $p_m = p_l$ , and (c)  $p_m = p_0 - [(p_0 - p_l)(x/l)]$ . If the membrane is porous and the species  $i$  is not molecularly dissolved in it, then the pressure distribution for the membrane and  $i$  may be different and case (c) would be likely to describe the distribution for  $i$  since transport would occur by viscous flow. The membranes of interest here are one-phase materials and the pressures on each species must be the same.

Determination of the pressure distribution within the membrane is a problem of mechanics. In principle, one can compute the complete stress tensor,  $\sigma$ , distribution throughout the membrane and then determine the membrane pressure distribution from the relation

$$p_m = -\frac{1}{3} \text{trace}(\sigma), \quad (5)$$

which is used to define the isotropic pressure. Kuhn<sup>15</sup> has considered such an approach to diffusion within molecular networks when stressed uniaxially. The problem of concern here involves the complication caused by the complex boundary conditions generated by the pores in the supporting plate, which introduce stresses within the plane of the membrane plus additional stresses in this plane generated by the mechanical restraint which keeps the membrane area constant. A complete and rigorous calculation would be very difficult; however, several limiting arguments can be used to show that  $p_m$  is equal to  $p_0$  throughout the membrane to a good approximation. The interesting experiment of Rosenbaum and Cotton<sup>14</sup> seems to be consistent with this. The distribution  $p_m = p_0$  will be used here. With it, a complete thermodynamic analysis and a mathematical model for calculation purposes will be developed. Using  $p_m = p_0$ , the chemical potential of  $i$  anywhere within the membrane may be written as

$$\mu^m_i = \mu^0_i + RT \ln a^m_i + V_i(p_0 - p_r), \quad (6)$$

provided the partial molal volume of  $i$  in the membrane is equal to  $V_i$ . At both surfaces, equilibrium should exist between  $i$  just inside the membrane and  $i$  in the adjacent solution; hence,  $\mu^s_{i0} = \mu^m_{i0}$  and  $\mu^s_{il} = \mu^m_{il}$ . Application of these conditions to eqs. (1), (2), and (6) gives the following connection between the activities in the solutions and just within the membrane:

$$a^m_{i0} = a^s_{i0} \quad (7)$$

$$a^m_{il} = a^s_{il} e^{-V_i(p_0 - p_r)/RT} \quad (8)$$

The application of pressure does not change the activity of  $i$  within the membrane at  $x = 0$ ; however, it does decrease the activity of  $i$  in the membrane at  $x = l$ . This is a central point in this theory.

The next task is to relate the activity of  $i$  within the membrane to the concentration of  $i$  via a suitable swelling theory. This will permit us to calculate the actual concentration difference across the membrane. From this point forward it will be convenient to speak specifically in terms of the case studied here, i.e., pure solvents, rather than the general multicomponent treatment followed up to this point. This means setting  $a^s_{i0}$  and  $a^s_{il}$  equal to unity. This single liquid will be designated as  $i = 1$ . The concentration of liquid in the membrane at  $x = 0$  can be measured directly since, according to the theory, it is unaffected by the upstream pressure. It will be convenient to express this as a volume fraction which will be designated  $v_{10}$ . The volume fraction of liquid in the membrane at  $x = l$ ,  $v_{1l}$ , cannot be measured directly, but it can be calculated if a suitable theory of network swelling is used.

The theory used here is that described by Flory.<sup>16</sup> The free energy change for swelling a polymer network of volume  $V_0$  with  $\bar{n}_1$  moles of solvent is composed of two parts, i.e.,

$$\Delta G = \Delta G_m + \Delta G_{el}. \quad (9)$$



The mixing part can be represented adequately by the well-known Flory-Huggins theory, i.e.,

$$\Delta G_m = RT[\tilde{n}_1 \ln v_1 + \chi_1 \tilde{n}_1 v_r], \quad (10)$$

where  $\chi_1$  is an empirical interaction parameter and  $v_r$  is the volume fraction of rubber (membrane material). The elastic part is assumed to be represented by the results of rubber elasticity theory as given by Flory, i.e.,

$$\Delta G_{el} = \frac{RT\nu_e}{2} [\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3 - \ln \alpha_x \alpha_y \alpha_z], \quad (11)$$

where  $\nu_e$  is the moles of elastically effective chains in the volume  $V_0$ , and the  $\alpha$ 's are the factors by which the various physical dimensions are changed by swelling. If swelling is uniform in all directions, then  $\alpha_x = \alpha_y = \alpha_z = v_r^{-1/3}$ . From these considerations the activity can be related to  $v_r$  by

$$\ln a^{m_1} = \ln(1 - v_r) + v_r + \chi_1 v_r^2 + \left[ V_1 \frac{\nu_e}{V_0} \left( v_r^{1/2} - \frac{v_r}{2} \right) \right] \quad (12)$$

which is, of course, a very well-known relationship. This equation can be applied to  $x = 0$  since the membrane is installed into the apparatus under these freely swollen conditions. For pure liquids,  $a^{m_{i0}} = 1$ , so we get

$$0 = \ln(1 - v_{r0}) + v_{r0} + \chi_1 v_{r0}^2 + \left[ V_1 \frac{\nu_e}{V_0} \left( v_{r0}^{1/2} - \frac{v_{r0}}{2} \right) \right]. \quad (13)$$

As a pressure is applied, the activity of 1 at  $x = l$  decreases according to eq. (8). Next, the volume fraction  $v_{rl}$  (hence  $v_{1l}$ ) will be related to this activity and thus to  $(p_0 - p_l)$ . The area of the membrane is restrained to be constant even though there are forces tending to shrink it. This means that

$$\alpha_y = \alpha_z = v^{-1/2}_{r0}. \quad (14)$$

The activity of 1 can then be computed from equations 9, 10, 11 and 14 properly accounting for this restraint. The result is

$$\ln a^{m_{1l}} = \ln(1 - v_{rl}) + v_{rl} + \chi_1 v_{rl}^2 + \left[ V_1 \frac{\nu_e}{V_0} \left( \frac{v_{r0}^{4/3}}{v_{rl}} - \frac{v_{rl}}{2} \right) \right] \quad (15)$$

which, combined with eq. (8), gives finally

$$\frac{-V_1(p_0 - p_l)}{RT} = \ln(1 - v_{rl}) + v_{rl} + \chi_1 v_{rl}^2 + \left[ V_1 \frac{\nu_e}{V_0} \left( \frac{v_{r0}^{4/3}}{v_{rl}} - \frac{v_{rl}}{2} \right) \right]. \quad (16)$$

Equation (15) is merely a vehicle by which we can calculate  $v_{1l}$ , i.e.,  $1 - v_{rl}$ , for a given  $a^{m_{1l}}$ . This equation holds no special significance to the ideas to be conveyed here. A purely empirical or a more sophisticated theo-

retical relation would serve the same purpose, provided it offers an adequate description of  $v_{1i}$  versus  $a^{m_{1i}}$ . This particular result is used because it is known to work well for the type of polymeric material used.

Evaluation of the parameters  $\chi_1$  and  $\nu_e/V_0$  and illustrative calculations of  $v_{1i}$  are considered later.

Two experiments have been reported in the literature which defend the theory embodied in eqs. (7) and (8) and the model summarized in eqs. (15) and (16). The first relates to the constancy of  $v_{10}$  as the pressure changes. Ham et al.<sup>17</sup> measured the equilibrium swelling of crosslinked polymers as a function of hydrostatic pressure and found the change to be extremely small for the pressures considered here. Their analysis shows that if  $\bar{V}_1^m = \bar{V}_1^s = V_1$ , there would be no change at all. The analysis given here has assumed this to be true, and surely it represents a quite good approximation. In view of these experiments we can be confident that  $v_{10}$  does not change as pressure is applied. The second relates to the calculation of  $v_{1i}$ . Gehman<sup>18</sup> studied what he called swelling pressures. A rubber network was enclosed in a rigid cell with porous walls through which a solvent could freely flow. The force generated as a function of the swelling was measured, and the results were represented quite well by equations similar in principle to that of eq. (16). This indicates that our prediction of  $v_{1i}$  should be reasonably good.

#### EVALUATION OF THE PARAMETERS $\nu_e/V_0$ AND $\chi_1$

Two parameters,  $\chi_1$  and  $\nu_e/V_0$ , appear in eq. (16) which must be evaluated to calculate  $v_{1i}$  by this equation. The density of elastically effective chains  $\nu_e/V_0$  can be determined by the theory of rubber-like elasticity from force-elongation experiments. The general theory<sup>19</sup> indicates that the stress based on the unswollen, unstressed cross-sectional area,  $\sigma_0$ , is

$$\sigma_0 v_r^{1/3} = (\alpha - \alpha^{-2}) \left( 2C_1 + \frac{2C_2}{\alpha} \right), \quad (17)$$

where  $v_r$  is the volume fraction of the rubber,  $\alpha = L/L_0$  ( $L_0$  being the unstressed length), and  $C_1$  and  $C_2$  are constants. The parameter  $C_1$  is independent of  $v_r$  and equal to the value derived from the Gaussian theory of rubber elasticity, i.e.,

$$C_1 = \frac{1}{2} \frac{\nu_e}{V_0} RT. \quad (18)$$

The parameter  $C_2$  is of unknown origin but is known to decrease as  $v_r$  decreases. Two experiments were performed with the rubber sheeting used here with the results plotted in Figure 5 in the manner suggested by eq. (17). In one experiment the rubber was unswollen, with  $v_r = 1$ ; while in the other, it was swollen by a low-vapor-pressure vacuum pump oil to  $v_r = 0.509$ . The latter experiment was run such that the composition remained constant. The low-vapor-pressure oil prevented such changes by evapora-

tion. The theory predicts the two curves should be linear, with a common intercept, but the swollen one should have a lower slope. These expectations are confirmed with the two intercepts being identical within 2%, which is within experimental error. The chain density was calculated from the average intercept to be  $\nu_e/V_0 = 1.06 \times 10^{-4}$  mole/cc.

Since  $\nu_e/V_0$  is known, the parameter  $\chi_1$  can be determined for each liquid from equilibrium swelling measurements via eq. (13). Equilibrium swell-

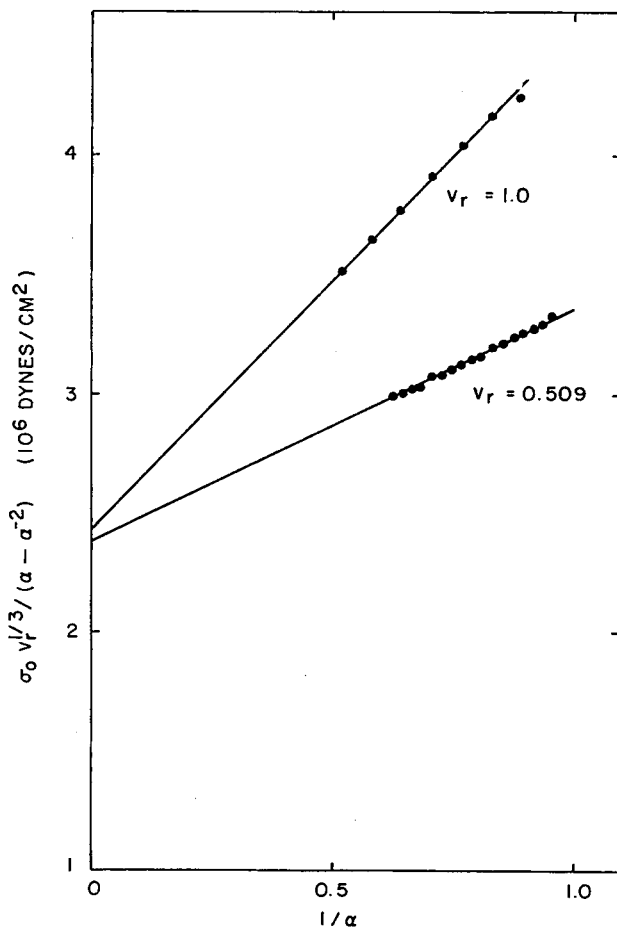


Fig. 5. Force-elongation data for determination of crosslink density.

ing measurements were made by weighing a dry sample of the rubber before and after equilibrium in each liquid. Density data (polymer = 0.97 g/cc) were used to compute from the gravimetric data the values of  $v_{r0}$  shown in Table I, which are accurate to about 0.002 volume fraction units. Values for  $\chi_1$  were computed using equation 13 with the results also shown in Table I.

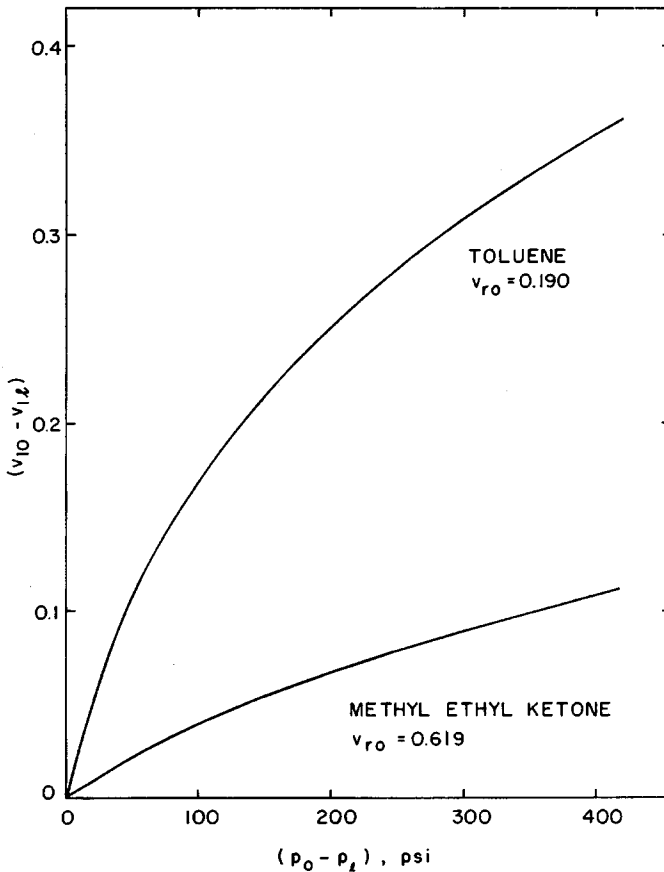


Fig. 6. Calculated differences in concentration across the membrane.

From these parameters and the known molar volume of each liquid,  $v_{1i}$  was computed for each liquid via eq. (16). Sample results for two liquids are shown in Figure 6 as  $(v_{10} - v_{1i})$  versus  $(p_0 - p_i)$ . These curves are quite similar in shape to the flux data in Figures 2-4. As one would expect, smaller differences,  $v_{10} - v_{1i}$ , are generated by a given pressure for less highly swollen networks.

In the next section, a diffusion theory is developed which relates the steady-state flux  $n_1 \hat{V}_1$  to the volume fraction difference  $v_{10} - v_{1i}$ .

### DEVELOPMENT OF A DIFFUSION THEORY

Fick's law of diffusion for a stationary coordinate system<sup>20</sup> is

$$\mathbf{n}_1 = \omega_1(\mathbf{n}_1 + \mathbf{n}_r) - \rho D \nabla \omega_1 \quad (19)$$

where the subscripts 1 and  $r$  refer to the solvent, or penetrant, and the rubber, or membrane material, respectively;  $\mathbf{n}$  = flux in mass units;  $\omega$  =

TABLE I  
Summary of Experimental Results (at 30°C)

Liquid	$V_1$ , cc/mole	$\eta$ , cp	$v_{r0}$	$\chi_1$	$a \times 10^2$ ,		$D \times 10^6$ cm <sup>2</sup> /sec
					$\frac{\text{cc}}{\text{cm}^2/\text{day}}$ psi	$b \times 10^3$ , $\frac{1}{\text{psi}}$	
Benzene	88.9	0.56	0.207	0.474	4.55	2.27	2.37
Toluene	106.0	0.53	0.190	0.425	5.72	4.52	2.36
<i>o</i> -Xylene	118.4	0.71	0.187	0.408	4.21	3.77	1.78
Tetralin	136.0	1.9	0.185	0.371	3.66	5.94	0.82
<i>n</i> -Hexane	130.8	0.29	0.337	0.587	5.63	3.92	4.06
<i>n</i> -Heptane	146.0	0.38	0.301	0.541	5.49	4.90	3.07
<i>i</i> -Octane	165.1	0.45	0.339	0.572	3.45	7.08	2.73
Cyclohexane	108.0	0.81	0.205	0.448	3.88	4.05	1.80
Cyclohexanone	98.4	1.82	0.281	0.551	2.80	13.65	0.66
Methyl ethyl ketone	89.1	0.38	0.619	0.891	1.06	4.20	4.09
Methyl isobutyl ketone	125.2	0.50	0.394	0.643	1.76	5.94	1.67
Carbon tetra- chloride	96.5	0.84	0.161	0.353	3.60	2.92	1.67

weight fraction;  $\rho$  = density of the polymer plus the solvent; and  $D$  = the diffusion coefficient. Species 1 diffuses in the  $x$ -direction only, and species  $r$  is stationary so that Fick's law may be reduced to

$$n_1 = -\frac{\rho D}{1 - \omega_1} \frac{d\omega_1}{dx}, \quad (20)$$

which is the usual form for diffusion through a stagnant layer. If there is no volume change on mixing as assumed earlier, eq. (20) can be rewritten in terms of volume fractions as follows:

$$n_1 \hat{V}_1 = -\frac{D}{1 - v_1} \frac{dv_1}{dx}, \quad (21)$$

where  $\hat{V}_1$  is the specific volume of the liquid, so  $n_1 \hat{V}_1$  is the volumetric flux used in Figures 2-4. If the diffusion coefficient is independent of concentration (an assumption which must be tested), then the concentration profile becomes

$$(1 - v_1) = (1 - v_{10}) \left( \frac{1 - v_{1l}}{1 - v_{10}} \right)^{x/l}, \text{ or } v_r = v_{r0} \left( \frac{v_{rl}}{v_{r0}} \right)^{x/l}, \quad (22)$$

which, combined with eq. (21), gives

$$n_1 \hat{V}_1 = \frac{D}{l} \ln \left( \frac{1 - v_{1l}}{1 - v_{10}} \right). \quad (23)$$

The term  $l$  is the actual membrane thickness under the conditions of the experiment. The thickness of the dry membrane is  $l_d$ , while the thickness

of the freely swollen membrane as it is placed in the cell is  $l_0$ . These two are related by

$$\frac{l_d}{l_0} = v_{r0}^{1/3}. \quad (24)$$

However, during diffusion there is a gradient of swelling, so  $l$  is less than  $l_0$  (in some cases as much as 40% less). The thickness of interest cannot be readily measured, but it can be calculated as follows: Since the area of the membrane is restrained to be constant, the following material balance for the rubber applies:

$$v_{r0}l_0 = \int_0^1 v_r dx. \quad (25)$$

Inserting the profile for  $v_r$  given by eq. (22) yields the true thickness,

$$\frac{l_0}{l} = \frac{v_{r1} - v_{r0}}{v_{r0} \ln \left( \frac{v_{r1}}{v_{r0}} \right)}. \quad (26)$$

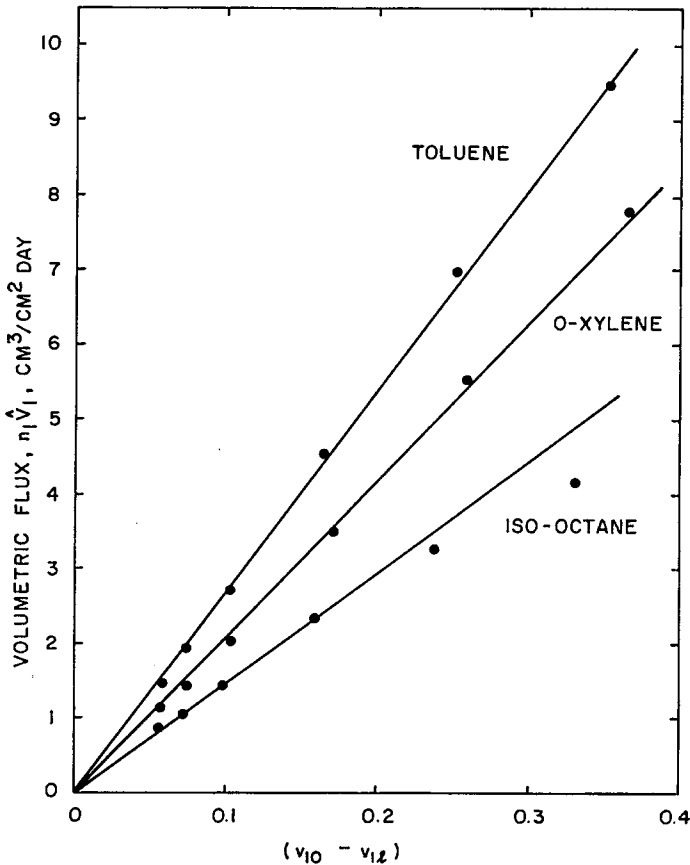


Fig. 7. Flux-concentration difference relationship.

The final diffusion result is obtained by combining eqs. (23), (24), and (26) and is most conveniently expressed as follows:

$$n_1 \hat{V}_1 = \frac{D}{l_d v_{r0}^{2/3}} (v_{10} - v_{1l}) \tag{27}$$

It predicts the flux to be directly proportional to the difference in volume fractions at the two surfaces, provided  $D$  is constant. Adherence to this prediction is examined next.

**EVALUATION OF DIFFUSION COEFFICIENTS**

A test of the thermodynamic and diffusion theories which have been developed can be made by comparison with the form of the experimental permeation results. This is done by plotting experimental  $n_1 \hat{V}_1$  values versus calculated  $(v_{10} - v_{1l})$  values from plots similar to Figure 6. According to the diffusion theory embodied in eq. (27), a straight line should result, provided of course that  $D$  is independent of  $v_1$ . Plots of this type are

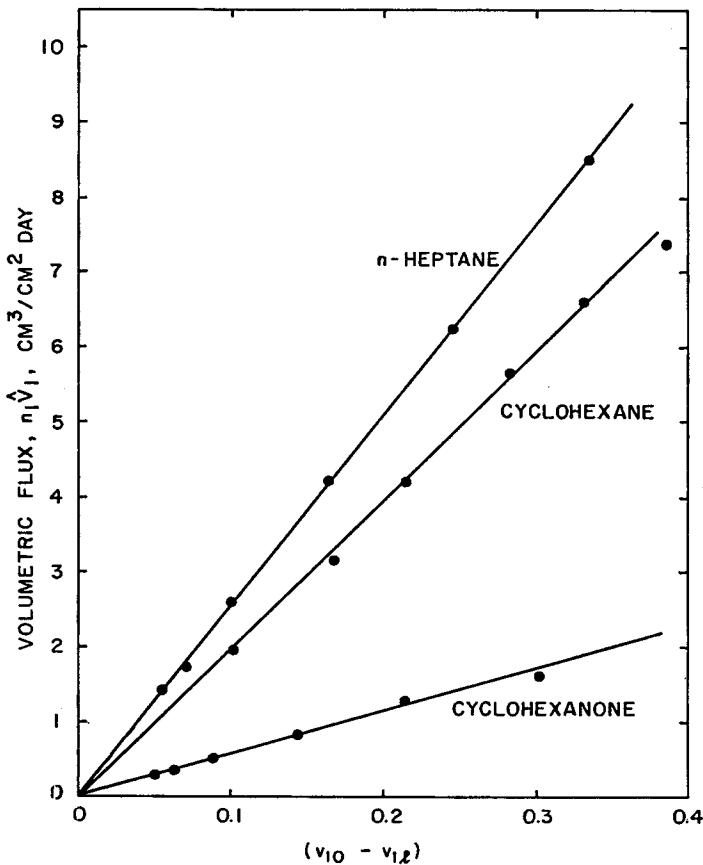


Fig. 8. Flux-concentration difference relationship.

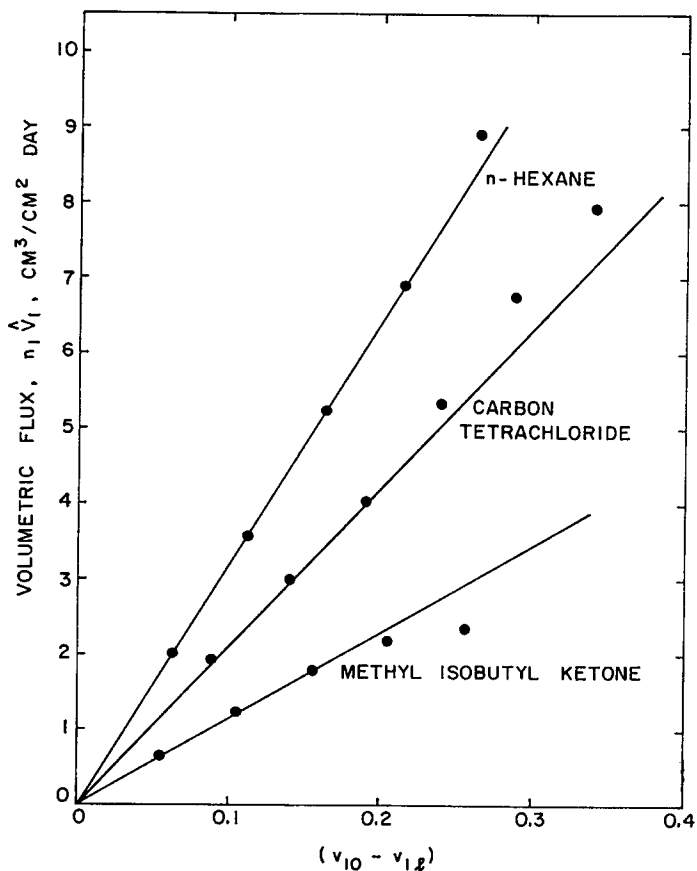


Fig. 9. Flux-concentration difference relationship.

shown in Figures 7-11, and for the most part remarkably straight lines are formed. This agreement in form strongly suggests that the theories embodied here are sound both quantitatively and in principle and that values of  $D$  deduced from the slopes of Figures 7-11 in accordance with eq. (27) are valid and meaningful transport coefficients. The resulting values of  $D$  are given in Table I for each of the 12 liquids.

Only five of the 12 liquids examined show any significant departure from linearity over the entire range of  $(v_{10} - v_{1z})$ , and in these cases there is an initial linear region followed by curvature at higher  $(v_{10} - v_{1z})$  values. Curvature may indicate merely a concentration-dependent  $D$ . Not many data are available for diffusion coefficients in polymers over an extensive concentration range, but those which exist<sup>21-23</sup> suggest that, for  $v_r$  near zero,  $dD/dv_r$  may be either positive or negative, while for  $v_r$  near unity  $dD/dv_r$  is always negative and very large. In the middle region of  $v_r$ , a plateau may exist where  $D$  is not very dependent on  $v_r$ . This plateau is the region where most of these experiments were performed, hence relatively



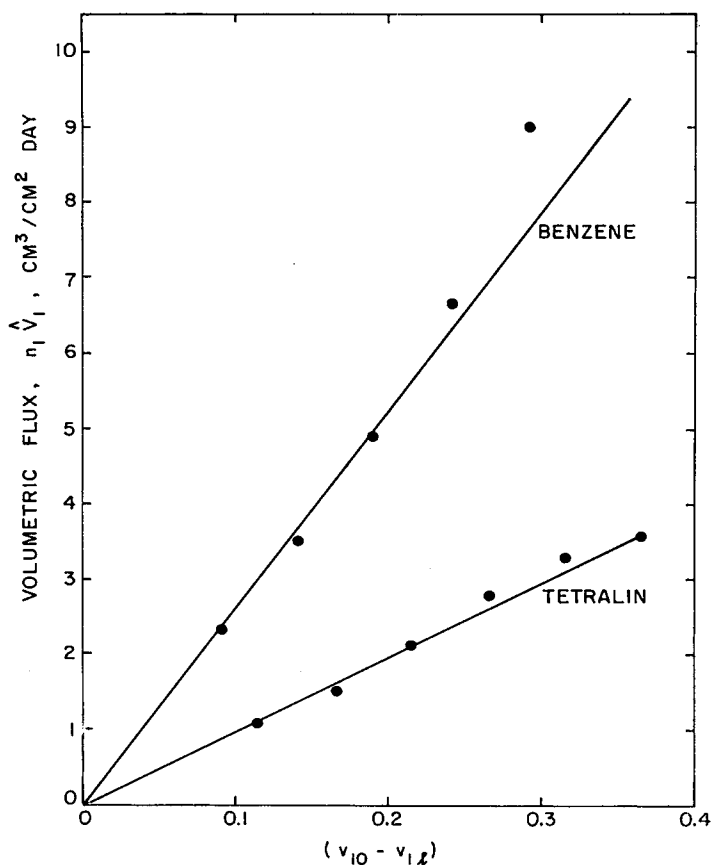


Fig. 10. Flux-concentration difference relationship.

constant values of  $D$  are not surprising. Three of the five, viz., isooctane, methyl ethyl ketone, and methyl isobutyl ketone, curve downward from the extension of the initial linear response. This is the direction expected if  $v_{1L}$  becomes small enough to cause an appreciable lowering of  $D$ . The upward curvature shown by benzene and carbon tetrachloride is not readily explained by any known concentration dependence of the diffusion coefficient. One possible explanation might be a concentration dependence of  $\chi_1$ . However, it is not worthwhile to belabor these points further at this time.

## DISCUSSION

An intriguing feature of pressure-induced transport through highly swollen membranes is the nonlinear relation between the flux and the pressure. For the thoroughly studied system cellulose acetate-water, the flux-pressure relationship has been shown to be linear,<sup>9,24</sup> barring possible compaction of a porous substructure which occurs in Loeb-

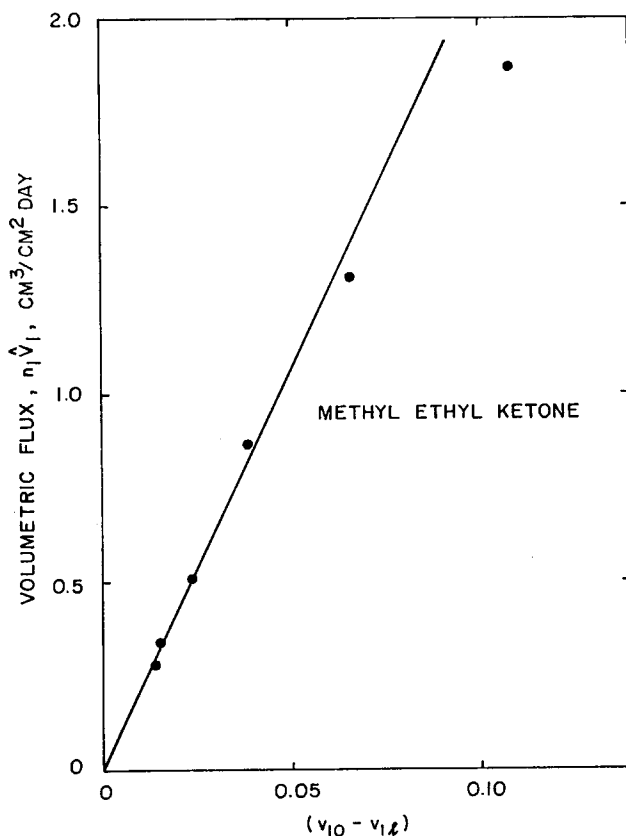


Fig. 11. Flux-concentration difference relationship.

type membranes. Diffusion theories that agree with this observation have been developed<sup>9,25</sup>; however, each formulation has been vague about the meaning of some terms. Inherent assumptions about the nature of the membrane pressure are not mentioned, and for this reason Rosenbaum<sup>13</sup> recently criticized these models. The final results of these theories, however, are essentially correct. Such laxness is permissible only because the change in concentration is small, and the final relation between the concentration differences generated and the pressure is linear. These are a consequence of the low degree to which water swells cellulose acetate. Clearly, a more detailed model must be specified to explain transport in highly swollen membranes where the concentration difference induced is not a linear function of pressure.

In the previous section, it was concluded that the transport coefficients evaluated from the experimental data are meaningful. It is now appropriate to ask what property of the liquid is most influential in establishing its value of  $D$  within this membrane. An analysis of the data given in Table I has revealed that in this case the viscosity of the pure liquid penetrant is

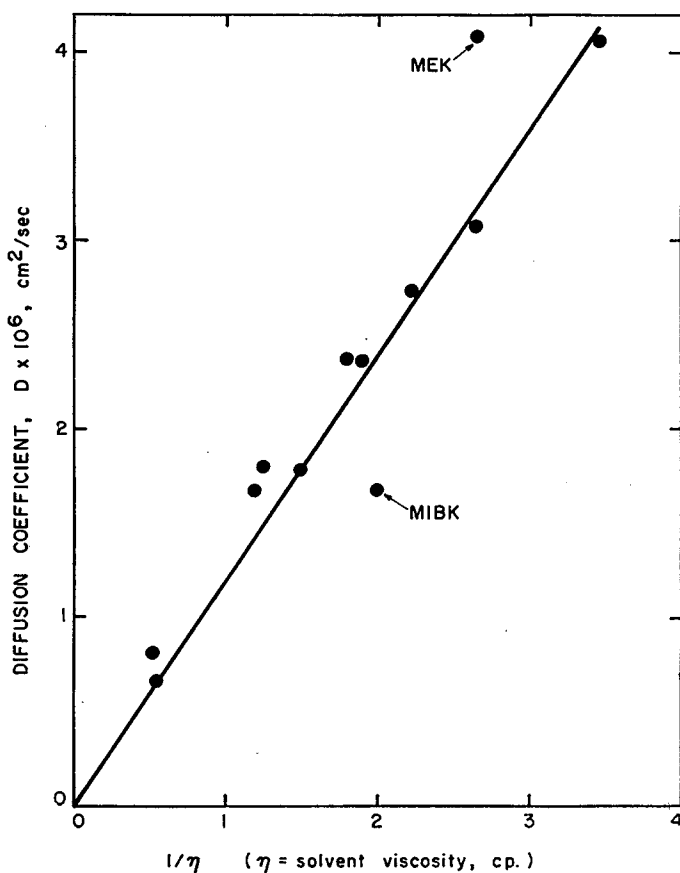


Fig. 12. Correlation of membrane-solvent diffusion coefficient with solvent viscosity.

apparently the single most important factor. Figure 12 substantiates this claim since all of the data, with the exception of two points, fall about a single straight line drawn on  $D$  versus  $1/\eta$  coordinates. The straight line drawn in Figure 12 holds no particular significance except to illustrate this trend. This result may be somewhat surprising, since we have maintained from the beginning that the mechanism of transport in this membrane is diffusive. However, there are many theories that attempt to relate diffusion coefficients to viscosity (e.g., see pp. 513–515 in Bird et al.<sup>20</sup>). Well-known examples include the theory of self-diffusion in liquids, the Stokes-Einstein equation for diffusion of large spherical particles or molecules in a solvent, and the Eyring rate theory. None of these theories, however, is exactly applicable to the situation of a solvent diffusing through a network of polymer chains that are restrained to no net macroscopic motion.

It is proposed that the current situation can be explained by an extension of the hydrodynamic theories of diffusion, a well-known example of which was given by Kirkwood and Riseman<sup>26</sup> for randomly coiled polymer

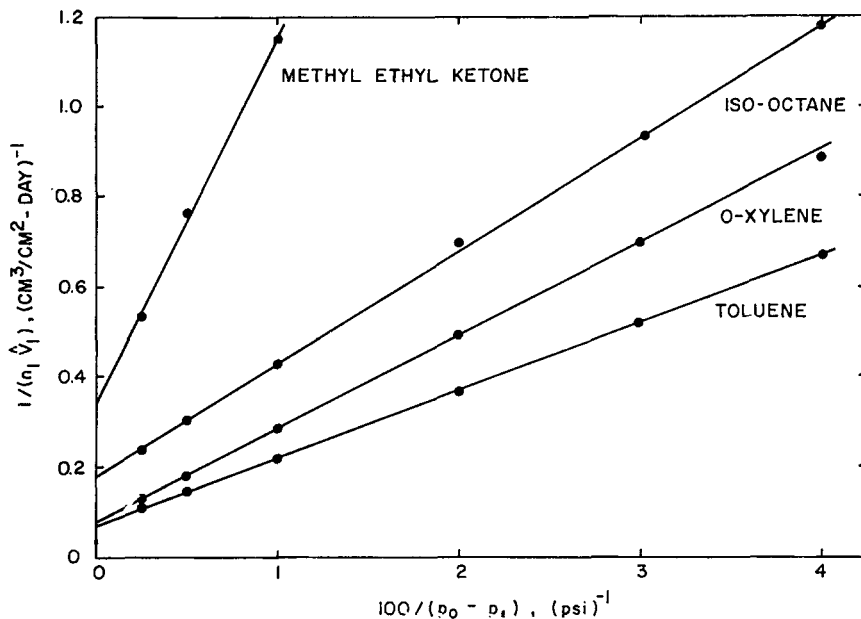


Fig. 13. Empirical reciprocal flux-pressure relationship.

molecules in dilute solution. The gist of such a theory would be to treat the forces arising from the relative motion of solvent past chain segments in the network as hydrodynamic in origin and proportional to  $\eta$ , the solvent viscosity. The forces are in turn related to the gradient of chemical potential that arises from the concentration gradient. Execution of this calculation would differ from the Kirkwood-Riseman treatment in that the chain segments are part of chains that form a three-dimensional network. At this point, it is judged that quantitative completion of this picture would be extremely difficult, so we will not pursue it further here. This exercise, however, does offer intuitive understanding as to how  $D$  may be proportional to  $1/\eta$  for a membrane. It is somewhat premature at this point to assert that the data in Figure 12 are exactly of this form. Two points on this graph depart markedly from the line drawn (these are methyl ethyl ketone and methyl isobutyl ketone). No explanation for these two points can be advanced except to note that these two swell the membrane appreciably less than any of the other liquids (compare  $v_{r0}$  values in Table I).

It is well known that, in many cases, it is the molecular size and shape of the penetrant molecule that determines  $D$ . This would more likely occur at very small penetrant concentration. Here, the transport rate is also controlled by the mobility of polymer segments. We might call this the *structural* regime of diffusion, whereas we might term the situation observed here as the *hydrodynamic* regime. It will be interesting to see if further work with liquids in polymers permits a classification into these two simple mechanisms of diffusion.

A very interesting empirical relationship between the flux and the pressure has been observed. Figure 13 illustrates for these cases that a very good straight line exists between the reciprocal of the flux and the reciprocal of the pressure. All of the liquids tested show this behavior. This dependence can be expressed by the equation

$$n_1 \hat{V}_1 = \frac{a(p_0 - p_i)}{1 + b(p_0 - p_i)}. \quad (28)$$

The constants  $a$  and  $b$  for each liquid are shown in Table I. The solid curves shown in Figures 2-4 were drawn using these constants and eq. (28). At this point, no fundamental significance is attached to eq. (28); however, it is interesting to note that this relation, if obeyed at very high pressures, means there is a ceiling flux which cannot be surpassed no matter how great the pressure. The idea of a ceiling flux is certainly plausible in terms of the theory developed here. The driving force  $(v_{10} - v_{1i})$  has a finite limit which cannot be exceeded. According to the theory,  $v_{10}$  is a constant, and  $v_{1i}$  is lowered as the pressure upstream of the membrane is raised; however,  $v_{1i}$  at best can be reduced to zero. In other words, the maximum driving force is  $v_{10}$ . Extrapolation of the straight lines in Figures 7-11 to  $(v_{10} - v_{1i}) = v_{10}$  gives in all cases a flux higher than the ceiling flux predicted by eq. (28), i.e.,  $a/b$ . This is reasonable, since it is known that  $D$  will decrease drastically as  $v_{1i} = 0$  is approached.

There is another way to arrive at the experimental conditions discussed here, i.e.,  $v_1 = v_{10}$  at  $x = 0$  and  $v_1 = 0$  at  $x = l$ . This may be done by having liquid above the membrane (no pressure need be applied) and a very good vacuum below the membrane. Since the activity of species 1 at the lower surface of the membrane is  $a_{1i}^m = p_1/p_1^* \cong 0$ , the value of  $v_{1i}$  will be very near zero, see eq. (16). This method of membrane operation has been called "pervaporation" by Michaels.<sup>6</sup> Thus, we may say that such a "pervaporation" flux would be the upper limit for any reverse osmosis flux. It would be interesting to determine experimentally whether these two modes of membrane operation are indeed related as suggested here.

Highly swollen membranes operated in a reverse osmosis fashion may be an attractive approach to effecting certain types of separations. For two reasons these membranes may be expected to yield high productivities. The first reason is that moderate pressures generate large differences in the concentration of swelling liquid across the membrane compared to less highly swollen ones. The effect of the degree of swelling is evident by comparing the different responses shown for methyl ethyl ketone ( $v_{r0} = 0.619$ ) and toluene ( $v_{r0} = 0.190$ ) in Figure 6. Both of these show concentration differences very much larger than those generated in the cellulose acetate-water system, where the equilibrium uptake of water is perhaps 10-15% by weight (totally dense cellulose acetate). An extreme example where the liquid is totally insoluble in the membrane further illustrates this point. Here, no concentration gradient can be induced by pressure, so no transport at all occurs. The second reason to expect high flux capability

is that in the highly swollen state the diffusion coefficient for the liquid is of the order of  $10^{-6}$  to  $10^{-5}$  cm<sup>2</sup>/sec rather than the  $10^{-9}$  to  $10^{-7}$  range typical in polymers swollen only slightly.<sup>21-23</sup>

The membrane employed in this work gave a toluene flux of about 2.5 gal/(ft<sup>2</sup>·day) at 400 psi. This is a very large flux when it is remembered that the dry thickness of this membrane was about 10 mils. A reduction in thickness to, say, 1 mil or less would bring the flux up to a level considered attractive for many separations. Actually, further reduction in thickness should not be too difficult.

However, to be useful in effecting separations, a membrane must pass one component much more rapidly than another. Generally, a high degree of swelling will result in less discrimination. The diffusion coefficients for all compounds will be larger in absolute magnitude in this state.<sup>27</sup> However, there are separations where adequate discrimination may exist. Examples are: removing the oil from oil-water emulsions, concentrating polymer solutions, and separating high molecular weight paraffin waxes from petroleum fractions. From both thermodynamic and transport considerations, it is expected that when the components of the mixture differ sufficiently in molecular size, separation should be easy. Of course, all methods of separations become easier when this is so; however, often there are advantages to a membrane process if it can be made competitive.

This work was supported by the National Science Foundation through Grant Number GK-3010. The help of M.D. Krasner in characterizing the membrane is gratefully acknowledged.

### Nomenclature

$a, b$	constants in eq. (28)
$a_i$	activity of species $i$
$C_1, C_2$	elastic constants
$D$	diffusion coefficient
$G$	Gibbs free energy
$l$	actual membrane thickness
$l_d$	thickness of dry membrane
$l_0$	thickness of freely swollen membrane
$L_0$	unstressed, swollen length of rubber
$L$	stressed length of rubber
$\mathbf{n}_i$	flux vector for species $i$
$n_i$	$x$ component of $\mathbf{n}_i$
$\tilde{n}_i$	moles of $i$
$p$	hydrostatic pressure
$p_r$	arbitrary reference pressure
$p^*$	vapor pressure
$p_m$	pressure in membrane
$R$	gas content
$T$	absolute temperature

$v_i$	volume fraction of $i$
$V_0$	volume of dry rubber
$V_i$	molar volume of $i$
$\bar{V}_i$	partial molal volume of $i$
$\hat{V}_i$	specific volume of $i$
$w_i$	weight fraction of $i$
$x, y, z$	coordinate axes

*Greek Symbols*

$\alpha$	extension factor
$\eta$	solvent viscosity
$\mu$	chemical potential
$\nu_e$	moles of elastically effective chains
$\pi$	osmotic pressure
$\rho$	density
$\delta$	stress tensor
$\sigma_0$	uniaxial stress based on unswollen cross section
$\chi_1$	Flory-Huggins interaction parameter

*Subscripts*

$i$	species $i$
$l$	conditions at $x = l$
$0$	conditions at $x = 0$
$r$	rubber or membrane
$x, y, z$	coordinate directions

*Superscripts*

$m$	membrane phase
$0$	reference state
$s$	solution, or liquid phase

**References**

1. R. N. Rickles, *Ind. Eng. Chem.*, **58**, No. 6, 18 (1966).
2. G. J. van Amerongen, *Rubber Chem. Tech.*, **37**, 1067 (1964).
3. J. Crank and G. S. Park, Eds., *Diffusion in Polymers*, Academic Press, New York, 1968.
4. E. J. Henley, N. N. Li, and R. B. Long, *Ind. Eng. Chem.*, **57**, No. 3, 18 (1965).
5. H. Z. Friedlander and R. N. Rickles, *Chem. Eng.*, **73**, 111 (Feb. 28, 1966).
6. A. S. Michaels and H. J. Bixler, in *Progress in Separation and Purification*, Vol. I, E. S. Perry, Ed., Interscience, New York, 1968, p. 143.
7. K. Kammermeyer, *ibid.*, p. 335.
8. A. S. Michaels, *Chem. Eng. Prog.*, **64**, No. 12, 31 (1968).
9. U. Merten, Ed., *Desalination by Reverse Osmosis*, M.I.T. Press, Cambridge, 1966.
10. C. Y. Choo, *Advances in Petroleum Chemistry and Refining*, Vol. 6, Interscience, New York, 1962, p. 72.
11. S. Sourirajan, *Nature*, **203**, 1348 (1964).

12. J. Kopeček and S. Sourirajan, *Ind. Eng. Chem., Proc. Des. Dev.*, **9**, 5 (1970).
13. S. Rosenbaum, *J. Polym. Sci.*, **6B**, 307 (1968).
14. S. Rosenbaum and Cotton, *J. Polym. Sci. A-1*, **7**, 101 (1969).
15. H. J. Kuhn, *J. Polym. Sci.*, **16C**, 859 (1967).
16. P. J. Flory, *Principles of Polymer Chemistry*, Cornell U. Press, Ithaca, 1953.
17. J. S. Ham, M. C. Bolen, and J. K. Hughes, *J. Polym. Sci.*, **57**, 23 (1962).
18. S. D. Gehman, *Rubber Chem. Tech.*, **40**, 532 (1967).
19. W. R. Krigbaum, *Rubber Chem. Tech.*, **38**, 1039 (1965).
20. R. B. Bird, W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena*, Wiley, New York, 1960.
21. S. Prager and F. A. Long, *J. Amer. Chem. Sci.*, **73**, 4072 (1951).
22. M. J. Hayes and G. S. Park, *Trans. Faraday Soc.*, **52**, 949 (1956).
23. A. Y. Chalykh and R. M. Vasenin, *Polym. Sci. USSR*, **7**, 642 (1965); **8**, 2107 (1966).
24. A. S. Michaels, H. J. Bixler, and R. M. Hodges, *J. Coll. Sci.*, **20**, 1034 (1965).
25. H. K. Lonsdale, U. Merten, and R. L. Riley, *J. Appl. Polym. Sci.*, **9**, 1341 (1965).
27. R. E. Pattle and P. J. A. Smith, *Trans. Faraday Soc.*, **62**, 1776 (1966).
26. J. G. Kirkwood and J. Riseman, *J. Chem. Phys.*, **16**, 565 (1948).

Received April 23, 1970

Revised May 22, 1970