

Hydraulic Permeation of Liquids Through Swollen Polymeric Networks. III. A Generalized Correlation

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Synopsis

An approximate equation was developed that permits calculation of the solvent tracer diffusion coefficient in a homogeneous swollen membrane from the measured hydraulic permeability coefficient. This relation was applied to data for 28 polymer-solvent systems that included 15 different organic solvents and 5 hydrocarbon polymer networks whose equilibrium swellings ranged from 16.1 to 91.5% polymer on a volume basis. The calculated tracer diffusion coefficient divided by the pure solvent self-diffusion coefficient for these systems formed a unique correlation when plotted versus the polymer volume fraction in the membrane. This relation agreed well with tracer diffusion coefficient data in the literature for the benzene-natural rubber system measured by radioactive tagging. Discussion centers on the evidence for the validity of the equation developed and the role of hydrodynamics on diffusion in swollen membranes.

INTRODUCTION

A number of earlier papers¹⁻¹⁰ were concerned with the diffusional transport of solvents across a membrane composed of a polymeric network swollen to various extents by the solvent. In this situation, one may define two diffusion coefficients for use in Fick's law which are experimentally accessible. These are the mutual diffusion coefficient D , which is applicable when the experiment involves an actual concentration gradient of the solvent within the membrane. The other is a tracer diffusion coefficient, denoted here by $D_1(v_1)$, which is the coefficient measured when there is not a gradient of the total concentration of the solvent but merely a gradient of a tagged fraction of this species. It was the emphasis of the earlier papers to deduce the *mutual* diffusion coefficient from hydraulic permeation data through the homogeneous, uniform swollen membranes. The calculation procedure has been adequately developed in the earlier papers, along with its application to a wide range of experimental data. The first two papers^{9,10} in this series had the specific purpose of applying this method of analysis to a range of experimental situations to gain further insight into the mechanism of diffusional transport through swollen networks and, in particular, to investigate the role hydrodynamics plays in determining transport coefficients.

Recently,⁶ an alternate method of analyzing hydraulic permeation was introduced which yields a transport coefficient that approximates the tracer diffusion coefficient $D_1(v_1)$. It is the purpose here to apply this approach to

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the hydraulic permeation results reported earlier and some new data presented here. The diffusion coefficients obtained by this route will be compared with extensive experimental measurements obtained via the tracer technique for diffusion of benzene in rubber membranes that traverse the entire spectrum of swelling levels.¹¹ The method of comparison will show that after proper accounting of hydrodynamic factors, specific for each individual solvent, the present results agree well with these experimental data for benzene. This close agreement offers strong support for the consistency of the hydraulic permeation data, the adequacy of the present method of analysis to give the tracer diffusion coefficient, and the importance of hydrodynamics in governing such transport.

EXPERIMENTAL

All of the systems of interest here were membranes made from hydrocarbon polymers in the form of crosslinked networks swollen by any of a wide variety of organic solvents. The level of swelling, denoted by the volume fraction of rubber in the membranes at equilibrium, v_{r0} , varied over a wide range because of the thermodynamic interaction of the solvent selected with the polymer, summarized here by the Flory-Huggins interaction parameter, χ_1 and the crosslink density of the network ν_e/V_0 .

Five different polymers, identified in Table I, were used. The first of these was already crosslinked and in membrane form as received. The other four, however, were pressed into film form and crosslinked for these studies. The polyisoprene polymer was crosslinked using a peroxide formulation, whereas the remaining ones employed a sulfur curing method. The details of the preparation have been described elsewhere.¹² The crosslinked density, ν_e/V_0 for each of these membranes was deduced from force-elongation measurements as described earlier.¹ Table II shows the organic solvents used with each of these membrane for hydraulic permeation measurements. There are a total of 28 different systems. Eighteen of these have been reported on previously, however, ten represent new results.

Special attention should be directed to the column headed v_{r0} , which indicates the volume fraction of rubber in the membrane at equilibrium swelling. Most of the ten new systems were selected to give low swelling levels since the earlier results fell primarily in the higher swollen region. Mutual diffusion coefficients have been reported for these 18 systems^{1,2,4} based on a method of analysis that recognizes the concentration gradient of solvent that is induced across the membrane by application of the hydrostatic pressure. This gradient was calculated from thermodynamic considerations. The flux for each

TABLE I
Membrane Materials

Polymer	Method of crosslinking	$\frac{\nu_e}{V_0}$, moles/cm ³
Natural rubber (gum sheeting)	Sulfur (as received)	1.04×10^{-4}
Butyl rubber	Sulfur	0.90×10^{-4}
Polybutadiene (Ameripol CB-220)	Sulfur	1.59×10^{-4}
Polyisoprene (Ameripol SN-600)	Peroxide	2.55×10^{-4}
SBR Rubber (Ameripol SBR-1013)	Sulfur	2.08×10^{-4}

TABLE II
Summary of Results for 30°C

Polymer	Solvent	v_{r_0}	$\left(\frac{\partial \ln a_1}{\partial \ln v_1}\right)$	$D_1(1) \times 10^5$, cm ² /sec	$D_1(v_{10}) \times 10^5$, cm ² /sec	$\left(\frac{\partial \ln a_1}{\partial \ln v_1}\right) \times 10^6$, cm ² /sec	$D \times 10^6$, cm ² /sec
Natural rubber	benzene	0.207	0.076	2.51	2.14	1.63	2.01
	toluene	0.190	0.091	2.50	2.09	1.90	2.00
	<i>o</i> -xylene	0.187	0.099	1.86	1.36	1.35	1.51
	tetralin	0.185	0.115	0.627	0.565	0.650	0.695
	<i>n</i> -hexane	0.337	0.098	4.25	2.98	2.92	3.44
	<i>n</i> -heptane	0.301	0.103	3.13	2.30	2.37	2.60
	isooctane	0.339	0.112	2.53	1.46	1.64	2.31
	cyclohexane	0.205	0.090	1.62	1.49	1.34	1.53
	cyclohexanone	0.281	0.080	0.745	0.610	0.488	0.466
	methyl isobutyl ketone	0.394	0.106	2.50	1.18	1.25	1.41
	carbon tetrachloride	0.161	0.099	1.62	1.25	1.24	1.41
	butyl acetate	0.322	0.097	1.92	1.41	1.37	1.30
	amyl alcohol	0.577	0.183	0.416	0.184	0.340	0.360
	2-ethyl-1-butanol	0.668	0.251	0.325	0.050	0.126	0.122
	diethyl carbonate	0.565	0.175	2.01	0.641	1.12	1.09
	Butyl rubber	<i>n</i> -hexane	0.296	0.088	4.25	3.98	3.50
<i>n</i> -heptane		0.253	0.096	3.13	2.16	2.07	2.20
isooctane		0.280	0.098	2.53	1.88	1.85	1.85
toluene		0.268	0.076	2.50	2.43	1.85	1.82
<i>o</i> -xylene		0.248	0.082	1.86	1.76	1.44	1.48
tetralin		0.219	0.094	0.627	0.542	0.509	0.390
cyclohexane		0.170	0.086	1.62	1.53	1.32	1.00
butyl acetate		0.710	0.338	1.92	0.225	0.761	0.624
diethyl carbonate		0.915	0.630	2.01	0.042	0.265	0.220
butyl acetate		0.388	0.134	1.92	0.966	1.29	1.33
Polybutadiene	diethyl carbonate	0.554	0.180	2.01	0.536	0.965	1.03
	toluene	0.201	0.193	2.50	2.10	4.05	4.06
Polyisoprene SBR	tetralin	0.187	0.212	0.627	0.403	0.854	0.915

pressure level was then plotted versus the calculated concentration differential. In general, the highly nonlinear plots of flux versus applied pressure became linear when flux was plotted versus the concentration differential. A reduction of Fick's law, including the important frame of reference terms, may be integrated across the membrane to show that such a plot should be linear when the mutual diffusion coefficient is independent of concentration, which is an adequate approximation if the concentration differential is not large. From the slopes of such plots the mutual diffusion coefficient can be deduced.

This method of analysis uses the experimental hydraulic permeation data for all pressure levels. The final column in Table II shows the mutual diffusion coefficient deduced in this manner for all 28 systems. The values entered here depart slightly from previously reported values for some of the systems owing to a recalibration of the active membrane area in the permeation cell. These values cover well over a decade in range and may be thought to be specific for the individual polymer, the solvent, and the degree of swelling. Part of the purpose of this paper is to sort out in a more detailed fashion this dependence.

CALCULATION OF $D_1(v_1)$ FROM THE HYDRAULIC PERMEABILITY

It was mentioned above and exhaustively shown in earlier papers that the relation between flux $n_1 \hat{V}_1$ and applied pressure Δp in hydraulic permeation experiments involving highly swollen membranes is quite nonlinear. Nevertheless, one may define phenomenologically a hydraulic permeation coefficient K from these data as follows:

$$n_1 \hat{V}_1 = K \left(\frac{\Delta p}{l_0} \right) \quad (1)$$

As noted earlier,^{1,5} the pressure dependence of K for most of these systems can be represented by the following empirical form:

$$K = \frac{K_0}{1 + b \Delta p} \quad (2)$$

In this equation, K_0 is the initial hydraulic permeation coefficient, while b is an empirical parameter to describe the pressure dependence of K . This equation has practical significance here since reciprocal plots of flux versus pressure can then be used to obtain a very accurate estimate of the initial hydraulic permeation coefficient K_0 which is more reliable than simply employing the initial slope of flux versus pressure plots. The method of analysis from this point forward will employ only the initial hydraulic coefficient K_0 and, therefore, does not use all of the data presented in a plot of flux versus pressure as the previous method of analysis did.

Earlier,^{5,6} we showed that the mutual diffusion coefficient D can be calculated from the hydraulic permeation coefficient K_0 as follows:

$$D = \frac{RTK_0(1 - v_{10})}{v_{10}V_1} \left(\frac{\partial \ln a_1}{\partial \ln v_1} \right) \quad (3)$$

where $v_{10} = 1 - v_{r0}$ and V_1 is the partial molal volume of the solvent (species 1). The derivative in parentheses expresses how the activity of the solvent in the membrane varies with the volume fraction of that species in the membrane evaluated at equilibrium swelling conditions. More will be said about this quantity later. Bearman¹³ has considered the possible relations between the measured mutual diffusion coefficient and the tracer diffusion coefficient from a theoretical point of view. For certain situations, this relation becomes

$$D = D_1(v_{10}) \left(\frac{\partial \ln a_1}{\partial \ln v_1} \right). \quad (4)$$

This is a widely recognized result that is often quoted and used in various calculations; however, it is not a rigorous result with universal applicability, as shown by several careful studies in liquid systems.^{14,15} If we combine this connection between the tracer diffusion coefficient and the mutual diffusion coefficient with eq (3), we obtain

$$D_1(v_{10}) = \frac{RTK_0(1 - v_{10})}{v_{10}V_1}. \quad (5)$$

Thus, we have a result for calculating $D_1(v_{10})$ from K_0 that does not require any thermodynamic information about the system, viz., the activity derivative. A similar relationship without the $(1 - v_{10})$ term in the numerator is used frequently in the literature.^{5,6} The term $(1 - v_{10})$ enters into this development from consideration of frame of reference terms in Fick's law which are very necessary and important in highly swollen systems as previously discussed.^{5,6}

Equation (5) has been used to calculate $D_1(v_{10})$ from the hydraulic permeation data for the 28 systems indicated in Table II with the results listed there in the fifth column. For a given system, these values are considerably larger than the mutual diffusion coefficients. Among the various systems, a range of more than a decade is covered. These coefficients will be subjected to further analysis in subsequent sections.

COMPARISON OF METHODS OF ANALYSIS

The values of the mutual diffusion coefficient shown in the last column of Table II were calculated by a graphic procedure that employed all of the data obtained in a hydraulic permeation experiment as indicated above and did not involve use of eq. (3) explicitly. The values of $D_1(v_{10})$ given in Table II, however, were obtained by use of K_0 values. It will be interesting to compare these two methods of analysis here. This may be done by comparing the D entries in Table II with the product $D_1(\partial \ln a_1 / \partial \ln v_1)$, since this should be the same result one would get if eq. (3) were used. To do this requires thermodynamic information about the system in order to obtain the activity derivative.

It would be interesting to employ detailed thermodynamic data of activity versus volume fraction to do this calculation; however, this information is not available for all of the systems of interest here. Therefore, as an alternate approach, we will employ the Flory-Huggins model for polymer solutions ap-

appropriately modified for network elasticity effects, which is well known to describe adequately swelling in such systems as reported here. The primary information inputs into this model are the crosslink density of the network, the molar volume of the solvent, and the degree of equilibrium swelling applicable for the system of interest. With this we can deduce the necessary parameters needed to estimate the desired derivative. It is important to remember that in the hydraulic permeation experiment, a fully swollen membrane is installed in the apparatus in a way which constrains the area of the membrane to remain constant even though the action of the pressure changes the level of swelling of the membrane. This fact must be properly accounted for in the thermodynamic model via appropriate modifications of the elasticity terms. From a previous paper, we showed that the relationship between the activity of solvent in the membrane under these conditions depends on the volume fraction of solvent in the membrane v_1 as follows:

$$\ln a_1 = \ln v_1 + (1 - v_1) + \chi_1(1 - v_1)^2 + V_1 \frac{v_e}{V_0} \left[\frac{v_{r0}^{4/3}}{(1 - v_1)} - \frac{(1 - v_1)}{2} \right] \quad (6)$$

where v_{r0} is the equilibrium swelling of the membrane and is the swelling level when the area of the membrane was fixed. It should be remembered in all that follows that the activity applies only to the membrane phase. This equation contains the following parameters which are experimentally known: V_1 , v_{r0} , and v_e/V_1 . The solvent interaction parameter χ_1 can be computed from the condition that $\ln a_1 = 0$ when $v_1 = 1 - v_{r0}$ and eliminated from eq. (6). The derivative of the resulting expression evaluated at $v_1 = 1 - v_{r0}$ gives the desired quantity:

$$\left(\frac{d \ln a_1}{d \ln v_1} \right) = 2 - v_{r0} + \frac{2(1 - v_{r0}) \ln(1 - v_{r0})}{v_{r0}} + V_1 \frac{v_e}{V_0} (1 - v_{r0}) \left[\frac{3}{v_{r0}^{2/3}} - \frac{1}{2} \right] \quad (7)$$

Since this equation contains only information that is experimentally available, the activity derivative can be calculated. Values for each system are shown in column 4 of Table II.

The value of $D_1(v_{10})$ for each system has been multiplied by the appropriate activity derivative to give the entry in column 7 of Table II. According to eq. (4), this quantity should be equivalent to the values of D given in the last column of Table II. As can be seen, the values in the two columns, while not always identical, are very similar in magnitude. In some cases the entry in the D column is larger than the entry in the $D_1(v_{10})(\partial \ln a_1 / \partial \ln V_1)$ column and smaller in other cases. As a statistical test, the ratio $D_1(v_{10})(\partial \ln a_1 / \partial \ln V_1) / D$ for the 28 systems were averaged. The mean value was found to be 0.99, with a standard deviation of 0.14. This demonstrates that the two quantities may be regarded from a statistical point of view as equal and any departures from equality in Table II are simply scatter.

It is important to recognize that the above is not really a test of the relationship given by eq. (4) but instead is a comparison of the consistency of two

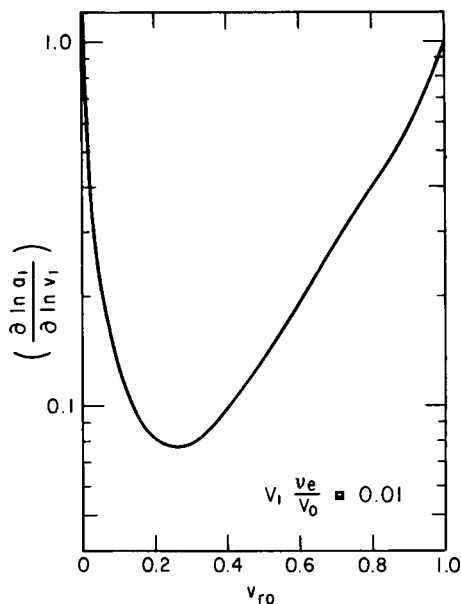


Fig. 1. Activity derivative evaluated at $v_1 = v_{10} = (1 - v_{r0})$ for a solvent-swollen network using eq. (7). Note that each point on the curve implies a unique value of the interaction parameter χ_1 .

methods of data reduction using the same principle. The calculation that yields D in Table II employed all the experimental flux data and might be regarded as an integral approach. The seventh column was calculated from $D_1(v_{10})$ using just the initial hydraulic permeation data plus activity information and may be regarded as a differential approach. It is interesting to note that, within the limits of experimental reliability of the various information, the two routes yield essentially the same results.

It will be of interest to consider further the activity derivatives employed in this calculation, since often it is necessary to make thermodynamic adjustments of mutual diffusion coefficient data^{16,17} in order to arrive at purely mobility-governed parameters. To investigate more fully the nature of the activity derivative for a crosslinked network, we have calculated the derivative as a function of equilibrium swelling level for a particular situation where $V_1(v_e/V_0) = 10^{-2}$. This would correspond, for example, to a membrane with $v_e/V_0 = 10^{-4}$ and solvents with $V_1 = 100$, which is typical of those systems reported here. The results of this calculation are shown in Figure 1. As v_{r0} approaches 1, the derivative becomes unity as one expects.^{6,17} The derivative decreases as the level of swelling increases; however, it goes through a minimum in the neighborhood of about 25% polymer and then increases to approach infinity as $v_{r0} \rightarrow 0$. This result is very unusual at first glance, since one normally might expect the derivative of activity to be a continuous monotonic function of concentration. However, it must be recognized that this plot does not show the effect of swelling level for a single polymer-solvent system, but instead each v_{r0} represents a different system with a unique value of χ_1 that will give this value of v_{r0} . As v_{r0} becomes smaller, the chains in the network are more highly extended and elasticity considerations make

progressively larger contributions to the derivative, which is the reason it approaches infinity as $v_{r0} \rightarrow 0$. For a given solvent-polymer system (fixed χ_1 value) of uncrosslinked chains or a network formed from a solution with polymer volume fraction v_r so that the chains are not strained, the following equation^{5,6,17} approximates the effect of polymer composition on the activity derivative:

$$\left(\frac{\partial \ln a_1}{\partial \ln v_1}\right) = v_r(1 - 2\chi_1 v_1). \quad (8)$$

Equation (8) reduces to the following special cases:

$$\begin{aligned} \left(\frac{\partial \ln a_1}{\partial \ln v_1}\right) &= v_r & \text{for } \chi_1 &= 0 \\ &= v_r^2 & \text{for } \chi_1 &= 1/2. \end{aligned} \quad (9)$$

It is clear from eqs. (8) and (9) that the activity derivative in this situation decreases in a monotonic fashion as the level of swelling increases and the derivative approaches zero (rather than infinity) as the polymer volume fraction goes to zero.

It is significant to note from Figure 1 that for a crosslinked network, the activity derivative goes through a minimum in the neighborhood of swelling produced by most good solvents for the natural rubber membrane employed in most of our earlier studies. Over a rather broad range of swelling levels from about 15 to 40% polymer, the activity derivative does not vary by more than a few per cent. This fact is important to the observation that the mutual diffusion coefficient was not concentration dependent for these systems since, as will be seen in the subsequent section, $D_1(v_{10})$ does not vary strongly in this region either. However, at lower levels of swelling, the mutual diffusion coefficient will depend on concentration more strongly since both $D_1(v_{10})$ and the activity derivative rapidly change in this region.

COMPARISON WITH TRACER MEASUREMENTS

The purpose of this section is to compare values of $D_1(v_{10})$ calculated from K_0 with literature values of the tracer diffusion coefficient for benzene in natural rubber reported by Pattle, Smith, and Hill.¹¹ Their measurements were made using radioactively tagged benzene molecules and covered the entire range from the self-diffusion coefficient of pure benzene $D_1(1)$ to the other extreme where very small amounts of benzene were present in the pure rubber, i.e., $D_1(0)$. It is clear that a comparison with all of the present data may not be made directly since the experiments here employ a wide range of liquids which have self-diffusion coefficients considerably different from those of pure benzene.

The value of the self-diffusion coefficient for a pure liquid is inversely proportional to the viscosity of that liquid and may be calculated by a formula of the following form:

$$D_1(1) = \frac{kT}{\sigma\eta} \left(\frac{N}{V_1}\right)^{1/3} \quad (10)$$

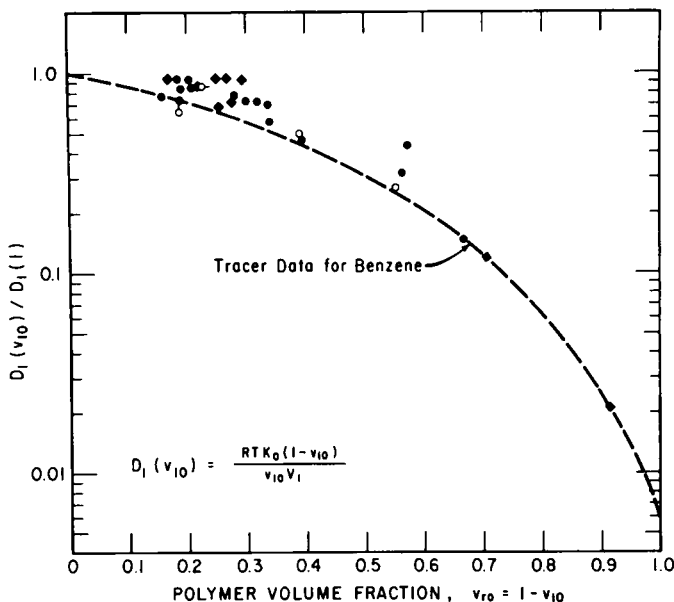


Fig. 2. Generalized correlation for solvent transport in rubbers. Points were calculated from hydraulic permeabilities while line represents tracer diffusion coefficients for benzene in natural rubber measured by radioactive tagging. Key to rubber types: (●) natural rubber; (◆) butyl rubber; (○) polybutadiene; (◻) polyisoprene; (◇) SBR.

where N is the Avogadro number, V_1 is the molar volume of the liquid, and η is the viscosity of that pure liquid. The parameter σ in the denominator is a constant for which a value of 2π is widely used,¹⁸ and in fact we used this value in an earlier paper.¹⁰ However, upon a more thorough analysis of self-diffusion coefficient data in the literature,¹⁹⁻²¹ it is clear that $\sigma = 4\sqrt{2}$ gives a better representation of most experimental data and will be used here. The latter value of σ gives self-diffusion coefficients which are approximately 11% larger than those using $\sigma = 2\pi$. Values of the self-diffusion coefficient calculated by eq. (10) are tabulated in column 5 of Table II. The considerable variation seen among these values derives principally from the difference in viscosity of the pure liquids.

As a strategy to compare the transport of various liquids through membranes in a single graph, we chose to plot the diffusion coefficient for a swollen rubber sample, $D_1(v_{10})$, divided by the self-diffusion coefficient for the pure liquid in question, $D_1(1)$, versus v_{r0} as shown in Figure 2. This approach has the effect of requiring all liquids to be normalized to a ratio of 1 in the limit of no polymer content. It has further justification through our earlier observation that mutual diffusion coefficients for a variety of liquids in swollen rubber were inversely proportional to the viscosity of the diffusing liquid which suggests a hydrodynamic regime of diffusion.^{1,4} Since the self-diffusion coefficient is also inversely proportional to the viscosity of the diffusing liquid, ratioing cancels this factor and leaves a parameter independent of liquid viscosity but dependent on the degree of swelling. The dashed line in Figure 2 is the experimentally determined tracer diffusion coefficient for

benzene reported by Pattle, Smith, and Hill.¹¹ Each point in Figure 2 represents data from Table II for a particular system, i.e., a particular rubber and solvent. Figure 2 is extremely striking since the points lie rather close to the dotted line for benzene.

We now wish to examine the meaning of this similarity of the two kinds of results and the possible underlying reasons. First of all, what would one expect to find if tracer measured diffusion coefficients through a single rubber for *different liquids* were compared by this kind of plot? If the diffusion of the liquid is governed principally by the rate of thermal movements within the liquid itself, that is to say, the movements of the solvent molecules are sufficiently more rapid than those of the polymer so that the chains act more or less as geometric obstructions, then one could expect all the $D_1(v_{10})/D_1(1)$ data to fall on a single curve versus v_{r0} in the region of high swelling since the magnitude of the obstruction effect should be a function of the volume fraction of polymer, v_{r0} . However, one would not expect the single plot for all liquids to apply in regions of very *low swelling* where solvent molecules are essentially isolated from one another by the polymer matrix. In this case, the viscosity of the liquid would not be the pertinent parameter to define the molecular motions that govern diffusion since polymer segmental motions should be the limiting factor. In addition, the molecular structure of the diffusing liquid should become an important factor which would obviate the possibility of a single curve applying in this region. In the high swelling region, the exact structure of the polymer (within a limited range of similar types) would be unimportant in determining its obstructing effect to the liquid transport. With this picture of diffusion, we can then expect to find that tracer-measured diffusion coefficients for many of the liquids and polymers shown in Table II would fall about a single curve of the type shown in Figure 2. However, it is uncertain how far toward the limit of pure polymer (where both the details of polymer and liquid structure would become important variables in determining the diffusion process) this should apply owing to the necessary cessation of the hydrodynamic regime of diffusion at some point. The points shown in Figure 2, however, are not tracer-measured coefficients but are estimations of this value obtained from hydraulic permeation measurements. The similarity of the present data with the dashed curve in Figure 2 then suggests the following two conclusions: (1) the hydrodynamic regime described above is operative, and (2) the present approach for estimating tracer diffusion coefficients from hydraulic permeation results is adequate. It is clear from the nature of this comparison that either both of these statements must be true, or there is some fortuitous cancellation of effects. In Figure 2, there is a high density of points in the high swelling region. There is some scatter among these points; however, the scatter is certainly no greater than the inherent experimental errors in the measurements and the calculation of the self-diffusion coefficient via eq. (10). Because of these cautions, it is only appropriate to examine the overall behavior in Figure 2 rather than the fine detail. Within this limit, we conclude that the dotted line for benzene agrees well with the points calculated from the present data (for a wide spectrum of systems obtained via a different kind of experiment) even though the latter appear to fall consistently above the line.

It is somewhat surprising to see that in the low swelling region beyond, say,

$v_{r0} \sim 0.5$, the limited hydraulic permeation data seem to continue to fall about the benzene line. We could not have predicted this a priori since at some v_{r0} , structural effects as mentioned above should begin to be important. The apparent agreement out to $v_{r0} \sim 0.9$ could be only fortuitous circumstances present in the few data points in this region. Data for solute transport through swollen membranes to be published later show that in the region $v_{r0} > 0.9$, diffusion is not controlled by hydrodynamic effects.

It is interesting to compare diffusion in natural and butyl rubber. It is well known that butyl rubber is a much superior barrier to gas transport than is natural rubber. In fact, diffusion coefficients for a wide variety of gases are approximately 20-fold smaller in butyl rubber than in natural rubber.²² However, the present data show that when the two rubbers are swollen by solvents, the differences in transport characteristics inherent to the pure rubbers is lost since data for the two rubbers fall on the same curve in Figure 2. This suggests that all polymer molecular motions in the swollen state are very sluggish in comparison to that of the solvent, even for natural rubber. This adds further confirmation to the idea that in the swollen state the polymer does not contribute to the diffusional process of the liquid by its molecular motions but instead acts as a barrier around which the solvent must diffuse.

CONCLUSIONS

The results shown here lead to three important conclusions:

First, we conclude that eq. (5) seems to give an adequate way of estimating the tracer diffusion coefficient from hydraulic permeation data. This is particularly significant since in many formulations of a similar equation, the term $(1 - v_{10})$ is not included. This factor, it will be recalled, stems from a consideration of frame-of-reference terms in Fick's law. Without it, the calculated tracer diffusion coefficient for a membrane with, say, $v_{r0} = 0.2$ would be five times larger than the values given by eq. (5). Such results would fall well above the curve for benzene in Figure 2 and might force one to conclude that diffusion is not the dominant mechanism of transport in hydraulic permeation. The close agreement shown in Figure 2 adds further confirmation to the fundamentally well-established fact that this term must be included.

Second, we conclude that to an adequate approximation, the mechanism of diffusion in highly swollen network polymers is governed by hydrodynamics. In this regime, the role of the polymer is principally to act as a barrier to the transport of the small solvent molecules. A similar point of view has been expressed in the form of a theory by Meares.^{23,24} At the present time, we are unable to establish the quantitative validity of this point of view or to place limits on the degree of swelling where such a regime applies. Clearly, in the limit $v_{r0} \rightarrow 1$, it must break down. The importance of hydrodynamics is only assured from the present results for relatively nonpolar systems. We have shown for the poly(vinyl alcohol)-water system that some aspects of a hydrodynamic regime are not present.⁹ This is not surprising in view of the strong polar interactions that exist between this solvent and polymer.

Third, we are in a position to better understand the correlation for swollen membranes observed in previous papers between the mutual diffusion coefficient and the solvent viscosity even though the level of swelling did vary over

a limited range. Certainly, to a limited approximation the mutual diffusion coefficient is the product of the tracer diffusion coefficient and the activity derivative as shown by eq. (4). Figure 1 shows that the activity derivative does not vary widely within the range $0.15 < v_{r0} < 0.4$. Correspondingly, Figure 2 shows that $D_1(v_{10})/D_1(0)$ does not vary greatly within these limits either. Thus, it is not at all surprising that the product $D\eta$ is nearly a constant to within, say, plus or minus 15% in this range of swelling.

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Nomenclature

v_1	volume fraction of solvent in membrane
v_{r0}	volume fraction of polymer in rubber membrane at equilibrium swelling
v_{10}	$(1 - v_{r0})$, volume fraction of solvent in membrane at equilibrium swelling
V_1	molar volume of solvent
D	mutual diffusion coefficient
$D_1(v_1)$	tracer diffusion coefficient of solvent in swollen membrane with solvent volume fraction v_1
$D_1(1)$	self-diffusion coefficient of pure solvent
K	hydraulic permeability coefficient defined by Eq. (1)
K_0	hydraulic permeability coefficient for small pressure differentials
χ_1	Flory-Huggins interaction parameter
$\frac{v_e}{V_0}$	polymer crosslink density
η	solvent viscosity
$\frac{\partial \ln a_1}{\partial \ln v_1}$	derivative of the logarithm of solvent activity with respect to the logarithm of solvent volume fraction evaluated at $v_1 = v_{10}$ and constant temperature and pressure

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