Solute Diffusion Through Swollen Polymer Membranes

D. R. PAUL, M. GARCIN, and W. E. GARMON, *Department of Chemical Engineering, The University of Texas, Austin, Texas 78712*

Synopsis

Experiments were designed to study the role of the solvent in the transport of a solute through a solvent-swollen polymer membrane. A single solute (an organic dye), a single polymer (cross-linked natural rubber), and 24 different organic solvents were used for this purpose. The solute diffusion coefficient D was calculated from the measured permeability P and distribution coefficient K, and was compared to the diffusion coefficient of the solute in the pure solvent. The main parameters of the solvent were shown to be its viscosity and the degree it swells the polymer. At high swelling, the results are in agreement with a model that pictures the resistance to solute diffusion as hydrodynamic interaction with the solvent while the polymer acts as an obstruction that increases the tortuosity of the diffusion path. At very low swelling, the diffusion coefficient approaches an asymptotic limit which is independent of solvent viscosity. However, even with as low as 10% solvent, some effects of viscosity are still seen. These results are discussed in terms of a quantitative theory for the obstruction effect proposed by Meares and compared to other literature data.

INTRODUCTION

The rate at which a solute diffuses through a polymer membrane is an important part of many processes of technological and scientific interest; and as a result, the literature contains numerous reports of experimental measurements of solute diffusion coefficients or permeabilities in membranes.[1-15] In general, the magnitude of the mobility or diffusion coefficient of a solute in a membrane, D, can depend on many factors. To date, the identity and influence of these factors have not been fully sorted out, in part because most research has employed systems of some particular interest rather than experiments designed to understand each individual factor.

It is the purpose of this paper to report some results from experiments selected for no other reason than to vary systematically some of these factors to understand more fully their effect. Inevitably, three components must be involved, viz., the polymer comprising the membrane, the solute, and a solvent. Hence, it is the chemical nature of each of these that determines the transport rate. The diffusion coefficient should depend on the degree to which the solvent swells the membrane, the nature of this solvent, the geometry of the solute, plus its interaction with the environment in the membrane.

For this work, it was decided that interesting results could be obtained by using the same solute and polymer but varying the solvent; and as an offshoot of other work,[16,17] a crosslinked rubber network polymer was selected whose

609

degree of swelling can be varied greatly depending on the choice of organic solvent. A nonionic dye was chosen for the solute because of the convenience of colorimetric analysis. While this dye is a relatively large molecule, it is small in comparison to the mesh size of the polymer network; and as a result sieving effects, while interesting, were not operative in these experiments.

For such simple systems, in which only the solvent is varied, one of the main variables clearly must be the degree to which this liquid swells the polymer; and to characterize this parameter, we will use the volume fraction of the polymer, v_{r0}, at swelling equilibrium. With good solvents where this fraction is small, the solute environment is largely solvent, and one could picture solute transport occurring through solvent-rich regions with the polymer chains simply acting as obstructions or causing a more tortuous path for solute diffusion.[16,18-22] In effect, this view considers solvent molecular motions to be considerably more rapid than those of the polymer.

In this model, the entire role of the polymer should be specified by v_{r0} since this determines the extent of the obstruction effect for all solutes and all polymers[20,21] in the absence of strong specific interactions between these two. An additional effect of the solvent choice, other than the v_{r0} it produces, is the rate at which solute can diffuse through this solvent in the absence of polymer. This rate of course depends on the nature of the solute as well and might be characterized by the diffusion coefficient of solute in the pure solvent, D_0, which can be measured experimentally but more conveniently can be estimated adequately by a number of pseudotheoretical equations of which the Wilke-Chang correlation[23] is a popular example:

$$D_0 = 7.4 \times 10^{-8} \frac{T(\psi_1 M_1)^{1/2}}{\eta V_2^{0.6}} \quad (1)$$

here D_0 has units of cm^2/sec, T is absolute temperature in °K, M_1 is the solvent molecular weight, η is the pure solvent viscosity in centipoises, V_2 is the solute molar volume in $cm^3/mole$, and ψ_1 is a solvent "association parameter" which is one for unassociated solvents. Other equations may be used to estimate D_0, but they give essentially equivalent results.[24,25] All of these correlations are based on the Einstein equation

$$D_0 = \frac{kT}{f} \quad (2)$$

with the friction coefficient f given by some empirical modification of Stokes' law, $f = 6\pi\eta R$, to estimate the effective solute radius R. As a result, the predominant factor in this latter effect is the pure solvent viscosity η. So, in this model, the main factors associated with a solvent choice in our experiments would be its thermodynamic interaction with the polymer that gives v_{r0} and its viscosity. One could extend this view into a specific mathematical model of the following form:

$$D = D_0 f(v_{r0}) \quad (3)$$

where $f(v_{r0})$ is a function that is always less than one except at $v_{r0} = 0$, where it is equal to one. Meares[20,21] has proposed the following theoretical expression for this function:

$$f(v_{r0}) = \left(\frac{1 - v_{r0}}{1 + v_{r0}}\right)^2 \qquad (4)$$

based on one approach to evaluating the obstruction effect described above.

Clearly, the simplistic view outlined above must break down at some level of swelling since in the limit of $v_{r0} \to 1$, the solvent must play no role at all. When there is no solvent present, the diffusional transport of the solute is entirely dependent on the segmental molecular motions of the bulk polymer which vary greatly from one polymer to another. One expects the effect of solute size, or structure, on the diffusion coefficient in a bulk polymer to be much greater than the $V_2^{0.6}$ term in eq. (1), which applies to pure solvent. At small but finite swelling levels, the role of the solvent is largely to plasticize the polymer, i.e., facilitate segmental motions, rather than to provide a medium for solute transport (which makes solvent viscosity a dominate factor). In earlier papers, this mode of transport was referred to as a structural regime while the mode where solvent viscosity is the main parameter was called the hydrodynamic regime.[16,17,22,26,27]

The purpose of the present study is to examine experimentally (1) the validity of eq. (3) for highly swollen membranes and its premise that the resistance to solute diffusion may be described as a hydrodynamic interaction with the solvent while the polymer acts as an obstruction; (2) the usefulness of eq. (4) to describe quantitatively the obstruction effect of the polymer; and (3) the level of swelling, v_{r0}, where this description breaks down and the motions of the polymer becomes more important than hydrodynamic interaction with the solvent.

SYSTEM SELECTION AND CHARACTERIZATION

The polymer selected was a commercially available sheet of lightly cross-linked natural rubber identical to that used in previous studies of solvent transport.[16] Its dry thickness l_d was 0.0275 cm. Twenty-four different organic solvents were selected on the basis of their ability to swell the polymer and their viscosity. Table I lists these solvents along with the equilibrium swelling of the polymer they produce, v_{r0}, and their viscosity η, both measured at 24°C except for the t-butyl alcohol, where 30°C was used. For the solute, the red dye known as Sudan IV (Color Index No. 26105, M = 380.4)
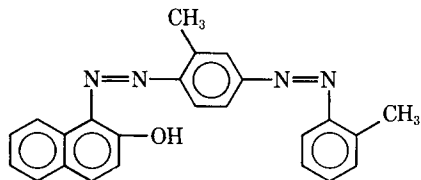
was chosen primarily because it is adequately soluble in the solvents selected. Its solubility in these liquids, C_S^L, was measured and is given in Table I.

Table I also shows the values of D_0 estimated by eq. (1) for this dye in each of the solvents. The molar volume of the dye, V_2, was estimated to be 275 cm³/mole using the method of LaBas.[28] The association parameter ψ_1 was taken to be one, except for the lower molecular weight alcohols, for which published values of ψ_1 were used.[23] Published comparisons of the Wilke-

TABLE I
Summary of Experimental Results[a]

Solvent	v_{r_0}	η, cp	C_s^L, mg/l.	$D_0 \times 10^6$, cm²/sec	K	$P \times 10^7$, cm²/sec	$D \times 10^6$, cm²/sec
Methanol	0.998	0.559	193	7.51	13.0	1.88	0.0145
Ethanol	0.995	1.13	141	4.10	6.31	0.915	0.0145
Isopropanol	0.961	2.22	131	2.26	7.47	1.17	0.0157
n-Propanol	0.901	2.0	272	2.51	4.39	1.46	0.0333
1-Butanol	0.897	2.57	289	2.04	3.48	1.49	0.0428
Acetone	0.889	0.318	1440	13.3	1.48	3.45	0.233
n-Pentanol	0.876	3.57	395	1.53	2.43	1.34	0.0550
Benzyl alcohol	0.872	5.91	4390	0.98	0.35	0.201	0.0582
2-Ethyl-1-butanol	0.758	5.3	460	1.07	2.5	1.99	0.0796
t-Butanol	0.719	3.35	280	1.56	4.88	6.40	0.131
t-Pentanol	0.676	3.67	263	1.49	2.95	5.22	0.177
Methyl ethyl ketone	0.609	0.403	1820	11.7	1.26	17.7	1.40
Ethyl acetate	0.57	0.441	663	12.2	1.03	12.8	1.24
Diethyl carbonate	0.565	0.747	785	8.33	0.84	7.22	0.854
n-Propyl acetate	0.405	0.551	696	10.5	0.92	20.6	2.24
n-Hexane	0.33	0.294	—	18.0	1.97	75.7	3.85
n-Heptane	0.301	0.386	3340	14.8	1.54	54.0	3.50
Cyclohexanone	0.22	1.98	2110	2.86	0.68	9.42	1.57
Cyclohexane	0.214	0.80	—	6.57	1.26	28.2	2.24
Toluene	0.195	0.552	1230	9.96	0.68	31.1	4.58
Tetrachloroethylene	0.189	0.87	—	8.48	0.78	25.9	3.29
Tetralin	0.181	2.00	1760	3.29	0.64	10.1	1.58
Trichloroethylene	0.163	0.55	—	11.9	0.72	34.0	4.69
Carbon tetrachloride	0.161	0.88	1760	8.07	0.84	21.9	2.62

[a] All entries are for 24°C, except for t-butanol which was evaluated at 30°C.

Chang equation with experimental data for similar systems indicate that we can expect the estimated values of D_0 shown in Table I to be within about 20% of the correct value on the average.[24,25]

As discussed earlier, we anticipate the main parameter for each solvent choice to be v_{r_0} and η. Ideally, we would like to vary them independently in order to isolate the effect of each; but strictly speaking, this is not possible because the solvent structure is responsible for both properties. However, we were careful in the solvent selection to avoid using a system of solvents where there existed a strong correlation between these two properties. Figure 1 shows a plot of $v_1 = (1 - v_{r_0})$ versus η for each of the solvents used, and in general a random pattern exists. There is, however, a tendency for the higher viscosity solvents to swell the polymer less. This stems from the fact that usually only solvents composed of large molecules have high viscosities, and for thermodynamic reasons large molecules are not good swelling agents. This fact limited the range of viscosities that could be employed in the high swelling region. Further, the only practical choice of liquids for the very low
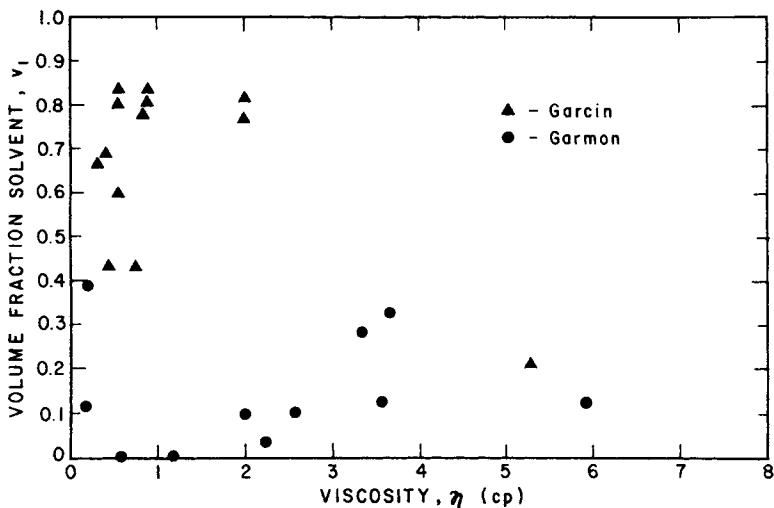
Fig. 1. Solvent properties. Each point represents a different solvent listed in Table I.

swelling region were alcohols, and one could expect a strong correlation between v_{r0} and η in a homologous series. The only way out of this dilemma is to use care in the interpretation of the results so as not to be mislead about what is an effect of v_{r0} and what is an effect of η.
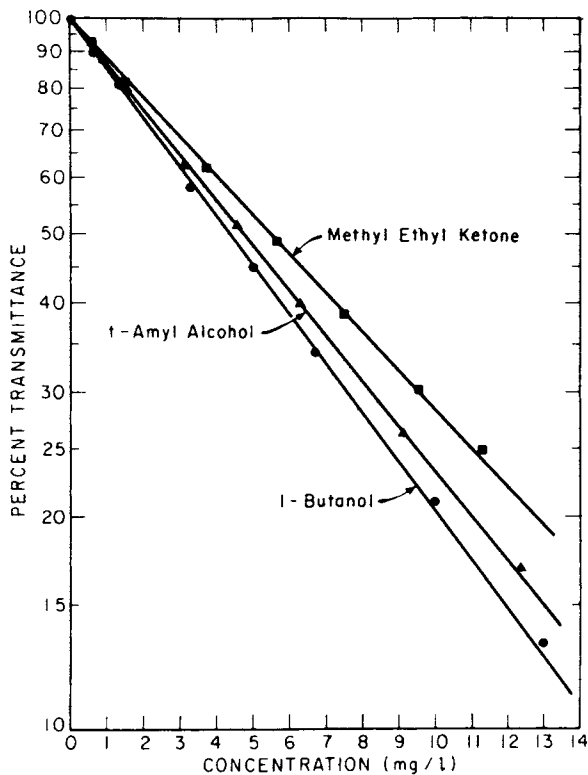

Fig. 2. Typical calibration curves for the dye Sudan IV in the solvents shown.

ANALYTICAL PROCEDURES

Colorimetric analysis was used to measure the concentration of dye in the organic solvents as needed during the course of the experiments described here. A Leitz photometer which required a 1.5-ml sample was used for this purpose. It was necessary to prepare a calibration curve for each solvent by measuring the per cent transmittance through prepared solutions of known concentration. Figure 2 shows sample calibration curves. Semilog plots gave linear calibrations, except at high dye concentration. All experiments were designed so that the dye solution to be analyzed had concentrations in a convenient portion of the per cent transmittance scale in order to insure accurate determinations. In some instances, very concentrated solutions were diluted by a known amount to bring the per cent transmittance into a sensitive range.

PERMEABILITY MEASUREMENT

The permeability of the dye through the swollen membrane, P, was measured using techniques similar to those of previous authors.[29-31] A schematic diagram of the cell especially designed for this work is shown in Figure 3. Because of the wide range of solvents employed, it was necessary to construct the cell of stainless steel. Stirring was provided by Teflon-coated magnetic stirring bars that were internally mounted as shown. Both bars were driven by a single magnetic stirrer turned on its side and rotated at 800 rpm. Both compartments had a volume V of 80 ml, and the membrane area A was 49.6 cm^2. Liquid samples were withdrawn from both sides at prescribed times for analysis and then returned to the cell. This operation required 2–3 min. The sample ports were closed except while withdrawing or returning liquid to avoid evaporation.
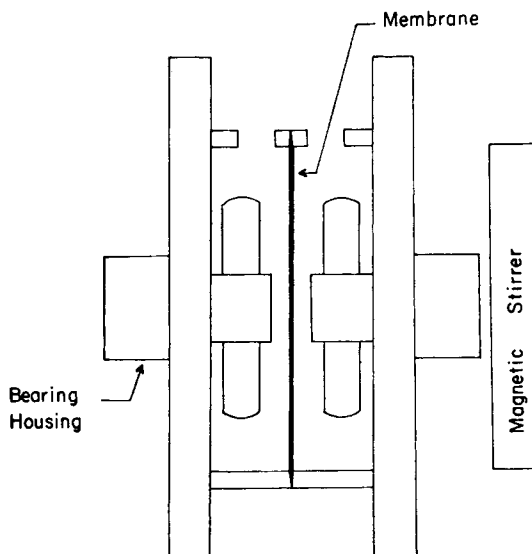

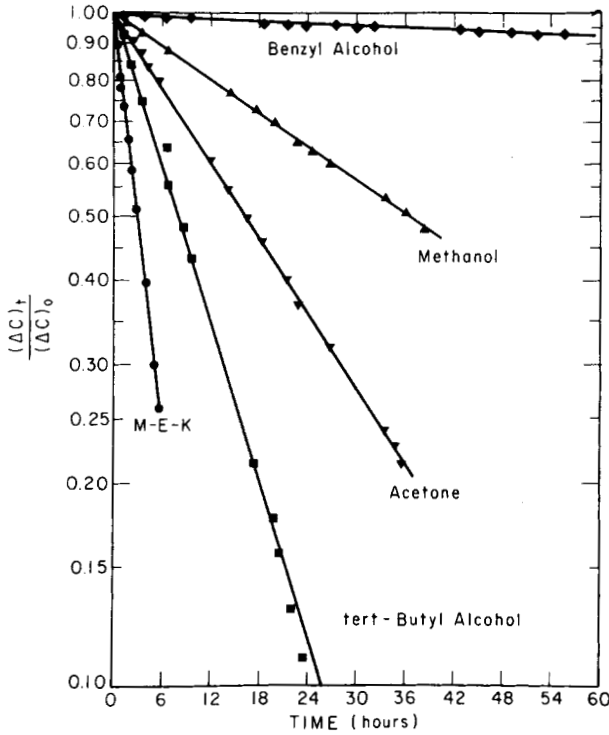Fig. 3. Schematic diagram of permeation cell. The two halves are held together by bolts not shown.

Fig. 4. Typical permeation data plotted in accordance with eq. (7).

The data analysis followed the conventional scheme for such experiments.[29-31] It was assumed that there was negligible osmotic liquid transfer, that the boundary layer resistance external to the membrane contributed negligibly to the total resistance, and that the dynamics within the membranes were very rapid so that a pseudosteady-state form of Fick's law could be used, i.e., the solute transfer rate J at any instant is given by

$$J = \frac{DA}{l} (C_2^m - C_1^m) \tag{5}$$

where C_2^m and C_1^m are the instantaneous solute concentrations inside the membrane at its surfaces adjacent to compartments 1 and 2. If we assume there is always equilibrium at the interfaces and the distribution coefficient K for the dye between the membrane and the solution is constant, we have

$$J = \frac{DAK}{l} (C_2^L - C_1^L) = \frac{PA}{l}(C_2^L - C_1^L) \tag{6}$$

where superscripts L denote concentrations in the external liquid phases. This result combined with a solute mass balance and subsequent integration yields the working equation

$$\ln \frac{(C_2 - C_1)_t}{(C_2 - C_1)_0} = \ln \frac{(\Delta C)_t}{(\Delta C)_0} = -\frac{PA}{2lV} t \tag{7}$$

where the subscripts t and 0 denote conditions at time t and $t = 0$. In all experiments, $(C_1)_0$ was made zero and both $(C_2)_t$ and $(C_1)_t$ were measured. Good material balance closures were always observed.

Figure 4 shows some typical data plotted in the manner suggested by eq. (7). Very good straight lines were always found. From slopes of these plots, the permeability P can be computed if l is known, since A and V have been specified. All of the membranes used were cut from the same sheet of rubber whose dry thickness l_d was very uniform. The membranes were preswollen to equilibrium in the solvent to be used and then installed in the cell in this state. Thus, the value of l in eq. (7) should be the swollen thickness which was computed from the following material balance relation which assumes isotropic swelling[16]:

$$l = l_d/(v_{r0})^{1/3}. \tag{8}$$

Table I lists the values of P determined for each solvent.

To test the reproducibility of the P values, multiple determinations of 4, 6, and 7 were made using three different solvents. The average absolute deviations from the mean values ranged from 1% to 3%; thus, the precision of the values in Table I should be better than 5%. The assumption about the boundary layer contribution was tested in two ways. These checks were made for solvents which highly swell the membrane and thus represent the worst case. First, the magnitude of the boundary layer effect was calculated from a published correlation scheme,[32] and this showed the contribution to be less than 1% at the stirring speed used. Second, the stirrer speed was reduced by a factor of 4 from the normal rate, and the permeability observed decreased only by 2% for one solvent and 4% for another. This agreed well with the calculated change using the correlation mentioned above. Thus, we conclude that the boundary layer effect is within or smaller than the precision limits of the experiment. Direct observation showed the assumption of no osmotic flow of solvent to be excellent.

DISTRIBUTION COEFFICIENT MEASUREMENT AND CORRELATION

The equilibrium partitioning of dye between a dye solution and the swollen membrane can be described by a distribution coefficient K, which should be a constant in the present systems.[24] This coefficient was measured by first immersing a preswollen sample of the polymer with volume v_m in an absorption bath consisting of a large quantity of a concentrated dye solution. Sufficient time was allowed for the dye to reach an equilibrium distribution between the polymer and the bath whose final concentration $C_a{}^L$ was then measured. Next, the polymer was transferred to a desorption bath consisting of a volume v_d of pure solvent where, again, enough time was allowed for the dye to equilibrate between the polymer and the bath. The final concentration of dye in this bath, $C_d{}^L$, was then measured. By a material balance and assumption of a constant K, the following equation may be derived:

$$K = \frac{C_d{}^L}{C_a{}^L - C_d{}^L} \frac{v_d}{v_m} \tag{9}$$
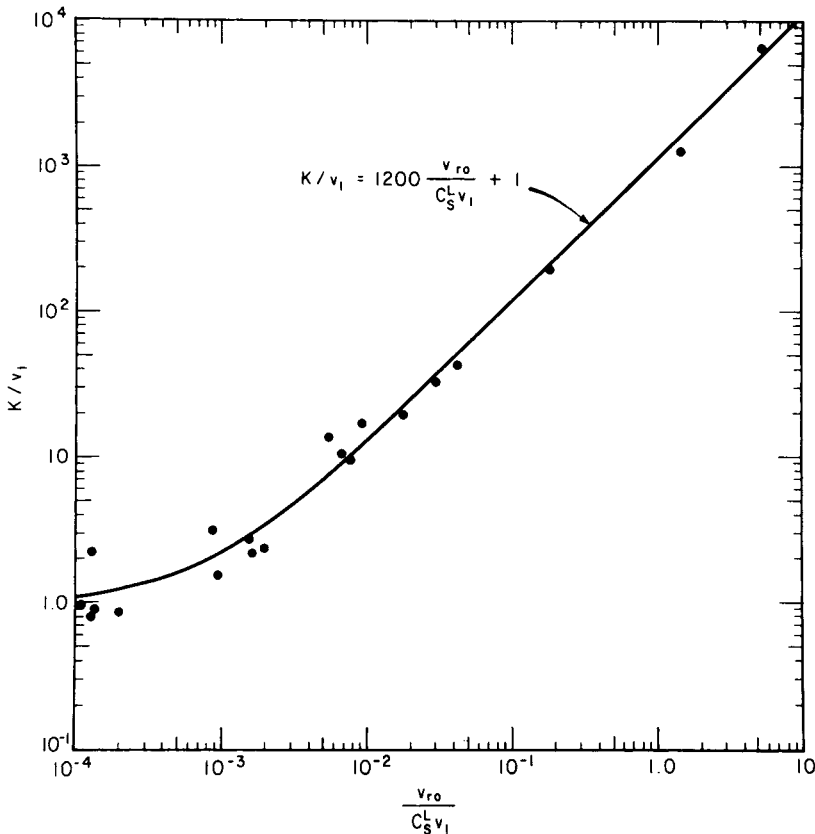
Fig. 5. Correlation of dye distribution coefficient. This method of plotting is suggested by eq. (13). The solid line was calculated from eq. (13), by arbitrarily assigning the unknown parameter $C_s{}^m$ a value of 1200 mg/l. to get the best fit of the data.

from which K can be computed since all parameters are known. Such measurements were repeated four times with each solvent, and the average deviation from the mean value was found to be less than 5%. In a few instances, experiments were designed to yield $C_d{}^L$ values that varied considerably and no trend was found in the computed K which gives evidence that it is indeed independent of dye concentration. The average K for each solvent choice is given in Table I.

It was noticed that K seemed to be related to the solubility of the dye in the solvent, $C_s{}^L$, and the equilibrium swelling, v_{r0}. It, therefore, seemed of interest to pursue such a correlation even though it would serve no useful purpose in the present work. A simple model was found to work very well and will be presented here simply as an aside. If K is a constant, then it must be equal to the ratio of the solubility of the dye in the swollen membrane (which consists of polymer plus solvent), $C_s{}^{(m+L)}$, to the solubility of the dye in the solvent, $C_s{}^L$:

$$K = \frac{C_s{}^{(m+L)}}{C_s{}^L}. \tag{10}$$

If the solubility of the dye in the swollen membrane is assumed to be an addi-

tive property of the solubility in the pure liquid, $C_s{}^L$, and the pure membrane, $C_s{}^m$, then

$$C_s{}^{(m+L)} = C_s{}^m v_{r0} + C_s{}^L v_1 \tag{11}$$

where $v_1 = 1 - v_{r0}$ is the equilibrium volume fraction of solvent in the membrane. Equations (10) and (11) can be combined to give

$$K = \frac{C_s{}^m v_{r0} + C_s{}^L v_1}{C_s{}^L} \tag{12}$$

or, in a rearranged form,

$$\frac{K}{v_1} = \frac{C_s{}^m}{C_s{}^L} \cdot \frac{v_{r0}}{v_1} + 1. \tag{13}$$

The latter suggests plotting K/v_1 versus $v_{r0}/C_s{}^L v_1$, which is done in Figure 5. A good unique relation results, and the line drawn was computed from eq. (13) with a value of $C_s{}^m = 1200$ mg/l.

CORRELATION OF THE DIFFUSION COEFFICIENTS

Since K and P are known, the diffusion coefficient of the dye in the swollen membrane, D, can be computed from the ratio P/K, with the results shown in Table I. Based on the error analyses for P and K, these values should not be
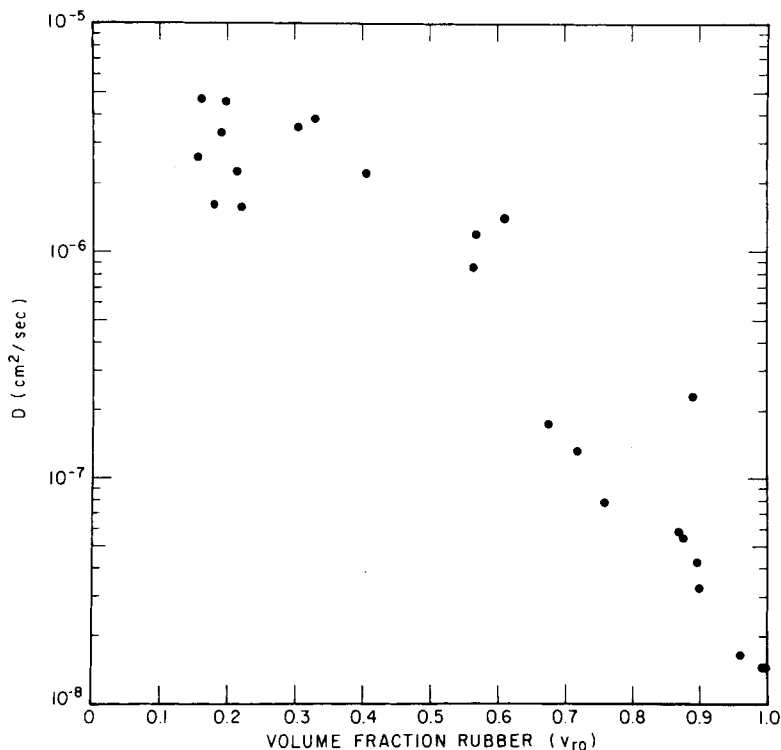

Fig. 6. Solute diffusion coefficients plotted vs. the fraction of polymer in the membrane at equilibrium swelling. Note that each point represents a different solvent.

in error by more than 10% in the worst cases, and generally the error should be less. Figure 6 shows D plotted versus v_{r0}. Since each point represents a different solvent, there should be no unique relation in this plot, although there is a general trend present owing to the large effect of v_{r0} on D.

It is now of interest to test the hypothesis stated in eq. (3). It should be reiterated that we expect this to break down in the limit of $v_{r0} \rightarrow 1$ so this region will be examined in another manner later. Equation (3) suggests plotting the data as D/D_0 versus v_{r0}, which is done in Figure 7. The combined errors in D and D_0 could make this ratio in error by as much as 30%, so we should not expect these results to form a precise relation even if eq. (3) is adequately descriptive of the situation. With this precaution, we conclude that Figure 7 does compress the data of Figure 6 into a fairly good relation for an amazingly large range of v_{r0}.

Perhaps the effect being discussed here could be made more clear in another way. Equation (3) predicts that if we selected several solvents of different viscosity (and thus different D_0) which swelled the membrane to exactly the same v_{r0}, D would be directly proportional to but less than D_0. Figure 8 attempts to show this graphically for seven solvents that swell the membrane to about the same extent, $v_{r0} \approx 0.20$, but not exactly. The line drawn has a slope of one, and the data fall about this line rather well. We thus feel that eq. (3) is a good approximation in the highly swollen region, but unfortunately the limitations on solvent choices do not permit a more extensive proof. From the present data, it is not possible to learn to what extent $f(v_{r0})$ might
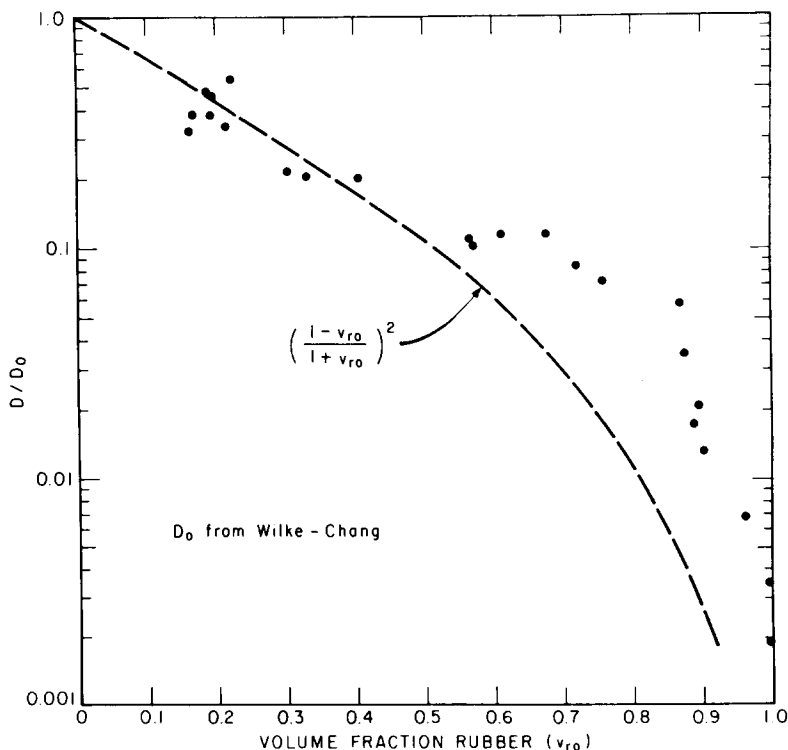

Fig. 7. Solute diffusion coefficient in swollen membrane relative to diffusion in pure solvent.
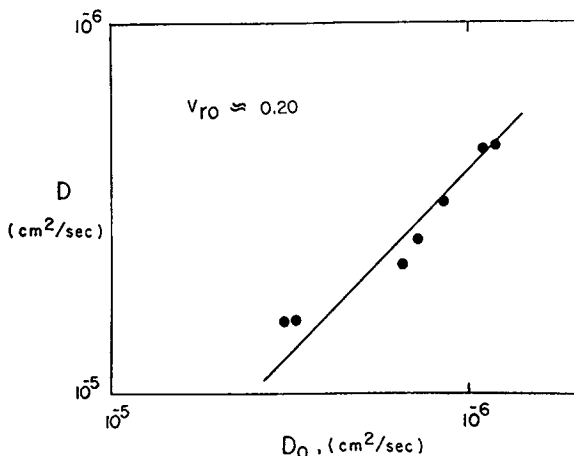
Fig. 8. Demonstration of proportionality of solute diffusion in swollen membranes to rate of diffusion in pure solvent. Each liquid used here swells the polymer by approximately the same amount.

be affected by the nature of the solute and the polymer since these have not been varied. Later, the meager literature data will be considered to further examine this point. It is interesting to note that Meares' proposal for $f(v_{r0})$, eq. (4), describes the present data very well out to a v_{r0} of about 0.5, after which it falls below the data. We can understand that this must happen at some point since it predicts D/D_0 to go to zero at $v_{r0} = 1$ because it ignores any contribution of polymer motions to the diffusion.

Equation (3) predicts that there should be a monotonic increase in D/D_0 to unity as v_{r0} goes to zero. On a gross scale our data in Figure 7 would agree with this although because of the crosslink density of our polymer even with the best solvents available v_{r0} could not be reduced to less than about 0.16. There are at least two sets of data in the literature[33,34] for widely different systems which suggest that D/D_0 goes through a maximum as v_{r0} is decreased.

To examine this point, we show our data in the high swelling range in Figure 9 using a logarimetic scale to stretch out the v_{r0} axis in this region for closer inspection. Also shown here are the data of Martin, Pattle, and Smith[34] for Oil Orange as the solute in natural rubber swollen by various solvents. Both their data and ours do seem to show a maximum although this observation is based on very few experimental data points. Similar maxima based on more data points have been reported for sodium and cesium ion self-diffusion in ion exchange resins[33] in about this same range of swelling. There are other fragmentary data available[24] which could be interpreted in terms of such a maximum. If it is real, this is a curious phenomenon indeed, because it suggests that at lower swelling there must be a minimum followed by a rapid rise as v_{r0} is decreased further since in the limit of $v_{r0} = 0$, D/D_0 has to become one. It is not possible to say more about this interesting possibility here, except that for our own data one might prefer to view Figure 7 on a more gross scale where the data in this region would appear as just slightly scattered. In view of the error limits on our data, we would not have felt jus-
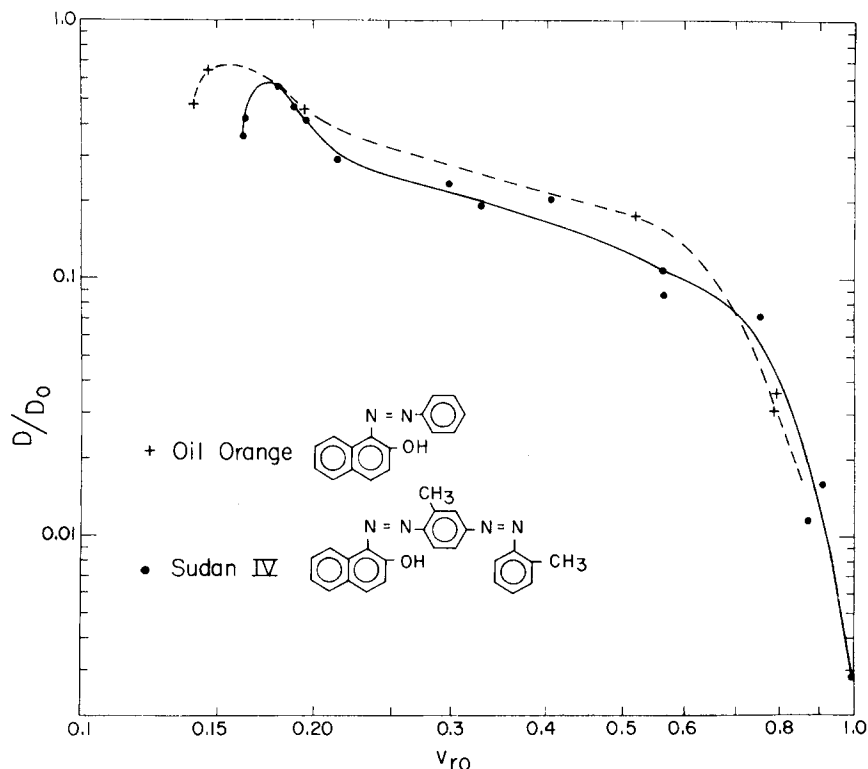
1.0

0.1

D/D_0

0.01

+ Oil Orange

N = N
OH

CH3
N = N   N = N
OH   CH3

• Sudan IV

0.1   0.15   0.20   0.3   0.4   0.5   0.6   0.8   1.0

v_{ro}

Fig. 9. Illustration of maximum in D/D_0 as a function of swelling.

tified in pointing out this possibility had it not been for the earlier observations.

We will now examine the low swelling end of the scale in another manner since Figure 7 does not give a proper insight into what is happening here. For reasons discussed above, the Meares equation predicts that D becomes zero in the limit $v_1 \to 0$; however, we should expect D to approach some finite limit that is independent of the solvent choice. The lower half of Figure 10, where D is plotted versus v_1 on a log–log scale permits us to examine this possibility for a series of alcohol solvents. The values of D obtained using methanol and ethanol (points 1 and 2) which swell the membrane very little are identical, and we believe this value is an asymptotic limit independent of solvent choice. Isopropanol (points 3), which swells the membrane to a larger amount, gives a D slightly above this limit. It is interesting to note from the upper half of Figure 10 that the D_0 for these three solvents are considerably different and decrease as one progresses up the alcohol series. This variation in D_0 appears to have no effect on D. We conclude, then, that in the range of v_1 from zero to about 0.04, there is no effect of the viscosity of the solvent on the dye diffusion process for this system. Beyond $v_1 \approx 0.05$, D rapidly increases, most likely because of the large plasticization effect since the general trend in D_0 is to continue decreasing.

Note that all of these solvents are alcohols except for point 8, which is acetone. As we increase the size of the hydrocarbon portion of the alcohol mole-

cule, the polymer is swollen to a greater degree but the solvent viscosity generally increases (D_0 decreases). The effect of the swelling seems to dominate the results rather than the viscosity. However, acetone provides an interesting comparison. It has a much lower viscosity (thus larger D_0) than the alcohols that produce equivalent swelling, $v_1 \approx 0.1$; and also the D for acetone is much larger. To see this, one should observe the relative positions of point 8 in the upper and lower halves of Figure 10. The swellings for acetone and 1-butanol are very nearly the same and thus allow a valid comparison. Their
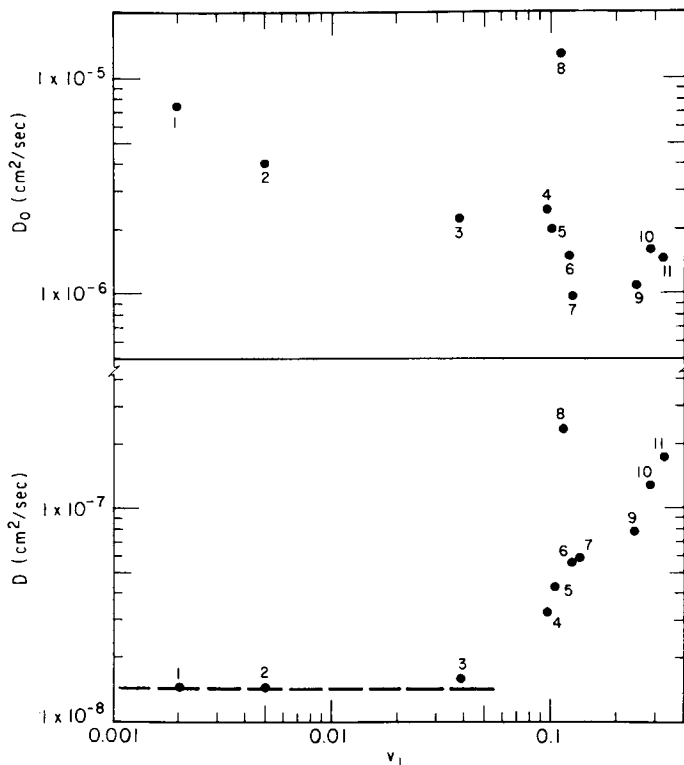

Fig. 10. Solute diffusion coefficient in swollen membrane (lower half) and pure solvent (upper half) for series of alcohols and acetone: (1) methanol; (2) ethanol; (3)isopropanol; (4) n-propanol; (5) 1-butanol; (6) n-pentanol; (7) benzyl alcohol; (8) acetone; (9) 2-ethyl-1-butanol; (10) t-butanol; (11) t-pentanol.

D_0 values form a ratio of 6.5, while their D values form a ratio of 5.4, which agrees with eq. (3). Unfortunately, the correlation between D_0 and v_{r0} that exists in the series of alcohols precludes saying more about the role of hydrodynamics in this region of swelling; however, we feel safe in concluding that there is some hydrodynamic effect at $v_1 = 0.1$ (as evidenced only by the acetone–alcohol comparison), whereas there seems to be no effect below $v_1 \approx 0.05$.

Equation (3) neglects any possibility for diffusion in the absence of solvent. Its usefulness might be improved if it were modified in some way to include this possibility. The simplest but crudest modification would view the struc-

tural and hydrodynamic regimes as parallel mechanisms, so that we may write

$$D = D_0 f(v_{r0}) + D_m \qquad (14)$$

where D_m is the value of D in the limit of $v_{r0} \rightarrow 1$. This suggests that we plot $(D - D_m)/D_0$ versus v_{r0} as shown in Figure 11, where for D_m we have used the asymptotic limit (dashed line) from Figure 10. The solid line is an arbitrary curve drawn by eye and could be said to represent the data adequately. The dotted line is $f(v_{r0})$ given by Meares and is an equally adequate representation for v_{r0} less than about 0.5. It should be noted that the points for
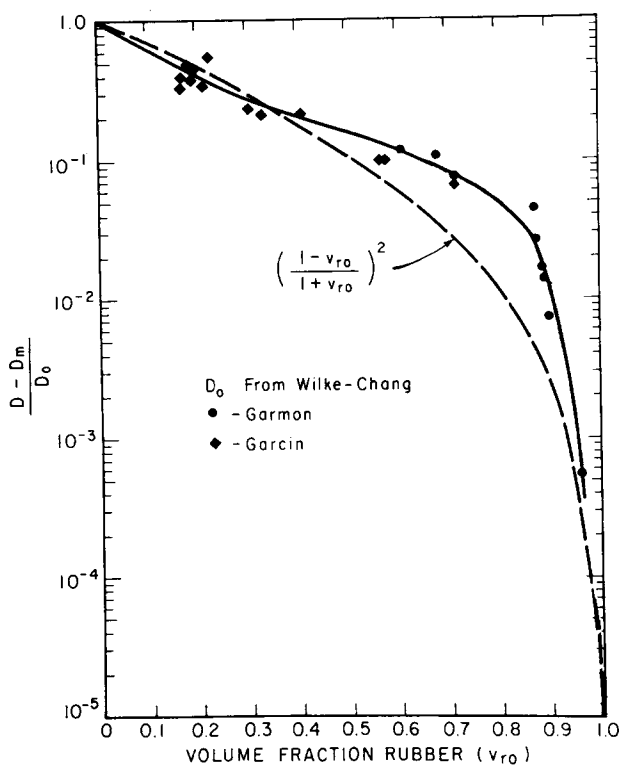

Fig. 11. Modified correlation to include diffusion rate in undiluted membrane.

methanol and ethanol appear at minus infinity on the ordinate since their D is equal to D_m.

Objections to eq. (14) can be raised. For example, in the limit of $v_{r0} \rightarrow 0$, D does not approach D_0, but rather it goes to $D_0 + D_m$. However, as a practical matter, D_0 will always be orders of magnitude larger than D_m. This and some other criticisms could be circumvented by writing eq. (14) as follows:

$$D = D_0 f(v_{r0}) + v_{r0} D_m. \qquad (15)$$

Because of the relative magnitudes of the D values involved, the location of the points in Figure 11 would not be altered to a detectable degree if this scheme of representation had been used.

SUMMARY AND DISCUSSION

The present work has employed a single solute and polymer and a variety of solvents to examine to what extent the diffusion of solute is influenced by the choice of solvent. Because of a number of complicating factors described here, it is difficult to generate a decisive picture of this situation. However, the facts seem to agree with the idea that in highly swollen systems the resistance to solute transport can be modelled in terms of hydrodynamic interaction with the solvent (with solvent viscosity being the main parameter) while the polymer acts chiefly as an obstruction to solute transport (with polymer volume fraction being the main parameter). Equation (3) formalizes this picture. Meares' theory for the obstruction effect seems to describe the present data quantitatively for polymer volume fractions less than 0.5, as well as data for some different systems reported in the literature.[21] This is interesting, since the Meares theory is not specific for the solute or the polymer neither of which were varied in our case. This would tempt one to conclude that $f(v_{r0})$ in eq. (3) is indeed independent of solute and polymer and is adequately represented by eq. (4), at least for high enough swelling.

However, we would like to point out some other data in the literature which have never been considered in this context. These data are presented in Figure 12 after normalization by D_0 as suggested by eq. (3). The solute, solvent, and polymer are identified in the figure (* denotes radioactively tagged molecules). The system labeled I is the very thorough benzene tracer measurements of Pattle, Smith, and Hill.[35] As can be seen, these data fall consistently above the Meares curve. Curve II for the dye Oil Orange[36] also
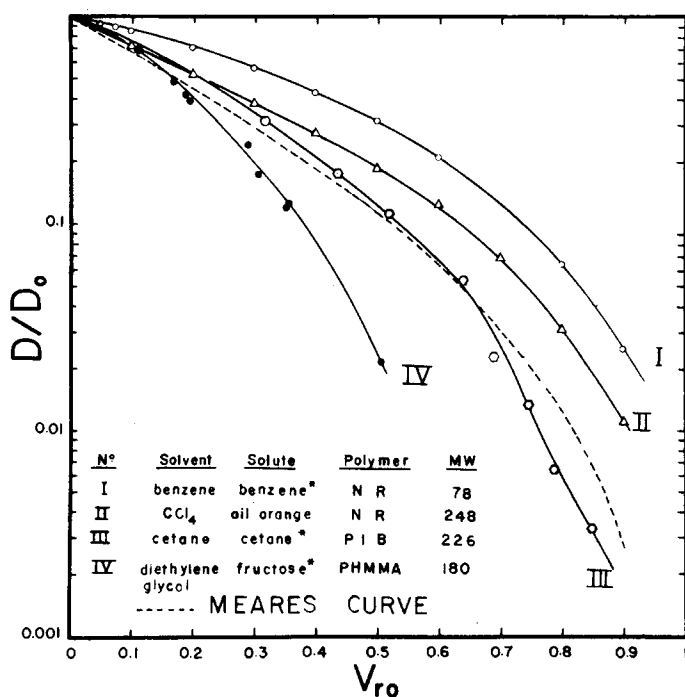

Fig. 12. Comparison of various literature data.

falls above the Meares line. The cetane tracer diffusion data,[37] on the other hand, could be said to be represented well by the Meares theory. Curve IV[38] falls well below the others. It is clear that the same function $f(v_{r0})$ does not represent all four systems. There are no obvious reasons why these systems should be different, e.g., the trend cannot be explained in terms of solute molecular size. Definitive conclusions in this area will have to be deferred until more detailed experimental work is available.

References

1. M. B. Rodel, W. L. Guess, and J. Autian, *J. Pharm. Sci.*, **55**, 1429 (1966).
2. H. Yasuda, *J. Polym. Sci. A-1*, **5**, 2952 (1967).
3. S. U. Li and J. L. Gainer, *Ind. Eng. Chem., Fundam.*, **7**, 433 (1968).
4. H. Yasuda, C. E. Lamaze, and L. D. Ikenberry, *Makromol. Chem.*, **118**, 19 (1968).
5. H. Yasuda, L. D. Ikenberry, and C. E. Lamaze, *Makromol. Chem.*, **125**, 108 (1969).
6. H. Yasuda, A. Peterlin, C. K. Colton, K. A. Smith, and E. W. Merrill, *Makromol. Chem.*, **126**, 177 (1969).
7. R. W. Coughlin and F. A. Pollak, *A.I.Ch.E. J.*, **15**, 208 (1969).
8. H. Yasuda and C. E. Lamaze, *J. Appl. Polym. Sci.*, **13**, 2209 (1969).
9. R. L. Riley, C. R. Lyons, and U. Merten, *Desalination*, **8**, 177 (1970).
10. H. Yasuda and C. E. Lamaze, *J. Macromol. Sci.-Phys.*, **B5**, 111, (1971).
11. M. P. Short and C. T. Rhodes, *Kolloid-Z. Z. Polym.*, **250**, 602 (1972).
12. S. K. Brauman and B. K. Fritzinger, *J. Appl. Polym. Sci.*, **16**, 2439 (1972).
13. H. D. Spriggs and J. L. Gainer, *Ind. Eng. Chem., Fundam.*, **12**, 291 (1973).
14. D. J. Lyman and S. W. Kim, *J. Polym. Sci.*, **41C**, 139 (1973).
15. G. L. Flynn, S. H. Yalkowsky, and T. J. Roseman, *J. Pharm. Sci.*, **63**, 3051 (1974).
16. D. R. Paul and O. M. Ebra-Lima, *J. Appl. Polym. Sci.*, **15**, 2201 (1970).
17. D. R. Paul and O. M. Ebra-Lima, *J. Appl. Polym. Sci.*, **15**, 2199 (1971).
18. A. L. Slade, A. E. Cremers, and H. C. Thomas, *J. Phys. Chem.*, **70**, 2840 (1966).
19. M. A. Peterson and H. P. Gregor, *J. Electrochem. Soc.*, **106**, 1051 (1959).
20. J. S. Mackie and P. Meares, *Proc. Roy. Soc. London*, **A232**, 498 (1955).
21. P. Meares, *J. Polym. Sci.*, **20**, 507 (1956).
22. D. R. Paul and O. M. Ebra-Lima, *J. Appl. Polym. Sci.*, **19**, 2759 (1975).
23. C. R. Wilke and P. Chang, *A.I.Ch.E. J.*, **1**, 264 (1955).
24. M. Garcin, M.S. Thesis, The University of Texas at Austin, 1973.
25. W. E. Garmon, M.S. Thesis, The University of Texas at Austin, 1975.
26. D. R. Paul, V. Mavichak, and D. R. Kemp, *J. Appl. Polym. Sci.*, **15**, 1553 (1971).
27. D. R. Paul, *J. Appl. Polym. Sci.*, **18**, 473 (1974).
28. R. C. Reid and T. K. Sherwood, *The Properties of Gases and Liquids*, McGraw-Hill, New York, 1966, pp. 86–89.
29. H. H. G. Jellinek and B. Blom, *J. Appl. Polym. Sci.*, **16**, 527 (1972).
30. R. P. Wendt, R. J. Toups, J. K. Smith, N. Leger, and E. Klein, *Ind. Eng. Chem., Fundam.*, **10**, 406 (1971).
31. G. L. Flynn and E. W. Smith, *J. Pharm. Sci.*, **60**, 1713 (1971).
32. K. A. Smith, C. K. Colton, E. W. Merrill, and L. B. Evans, *Chem. Eng. Prog. Symp. Series No. 84*, **64**, 45 (1968).
33. A. O. Jakubovic, G. J. Hills, and J. A. Kitchener, *J. Chim. Phys.*, **55**, 263 (1958).
34. R. A. M. Martin, R. E. Pattle, and P. J. A. Smith, *Trans. Faraday Soc.*, **66**, 2340 (1970).
35. R. E. Pattle, P. J. A. Smith, and R. W. Hill, *Trans. Faraday Soc.*, **63**, 2389 (1967).
36. R. E. Pattle and P. J. A. Smith, *Trans. Faraday Soc.*, **62**, 1776 (1966).
37. R. S. Moore and J. D. Ferry, *J. Phys. Chem.*, **66**, 2699 (1962).
38. C. P. Wong, J. L. Schrag, and J. D. Ferry, *J. Polym. Sci. A-2*, **9**, 1725 (1971).