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THE SOLUTION-DIFFUSION MODEL FOR SWOLLEN MEMBRANES

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INTRODUCTION

It has been widely recognized for many years that gases, vapors, liquids, and solutes permeate through non-porous polymer membranes by a solution-diffusion mechanism[1-5]. However, it was only ten years ago that it was first proposed[6] that reverse osmosis might be quantitively described by this mechanistic model. The solution-diffusion model first published by Lonsdale, Merten and Riley[6] has been applied with considerable success to describe a variety of systems but the cellulose acetate-water-inorganic salt system has received most attention due to its importance in desalination. It is widely accepted that this model not only describes the process of reverse osmosis but also represents an accurate mechanism in those cases where the membrane structure is truly dense, i.e. non-porous, with no imperfections - this condition refers only to the "active layer" in Loeb-type[6] membranes.

As it turns out, a major parameter in the hydraulic permeation of liquids through membranes by a solution-diffusion mechanism is the degree to which the liquid swells the membrane. The specific result obtained by Lonsdale, Merten and Riley (hereafter abbreviated as the LMR model) applies only in the limit of very low swelling levels but is quite adequate for the system cellulose acetate-water because the equilibrium swelling is of the order of 15% water. An inherent feature of this low swelling limit is mathematical linearity for all practical pressures, and this fact lends to many simplifications in the formulation. For higher levels of liquid solubility in the membrane, a more general model than the LMR result can be generated but it requires a more detailed accounting of events within the membrane demanded by the lack of linearity accompanying high swelling. Over the last five years the details of such a model have been published along with a wide spectrum of experimental data to support its validity[7-19]. The main objective of these papers[7-19] was to understand liquid transport in polymers when the degree of swelling varied widely no matter what external force was used to produce the transport. It is the purpose of this paper to 1) review briefly the concepts underlying this more general solution-diffusion model, 2) summarize some specific results that are applicable to membrane separation processes, and 3) present a useful scheme to estimate the hydraulic permeability of membranes when solution-diffusion is the mechanism of transport.

REVIEW OF THEORY

Pressure Generation of Concentration Gradient

The first problem we will consider is the hydraulic permeation of a pure liquid through a non-porous but swollen polymer membrane. If transport occurs by a solution-diffusion mechanism, then there must be a gradient in the concentration of this liquid within the membrane induced by the applied hydrostatic pressure. We now consider why this gradient is induced, and how we can predict its magnitude. It is convenient to express the liquid content in the membrane as a volume fraction, v_1. At equilibrium the liquid content will be uniform throughout the membrane at a value v_1^*. In the hydraulic permeation experiment, the membrane rests on a porous support as shown in Fig. 1, and the upstream liquid is pressurized to a level p_o while the downstream liquid remains at a pressure p_ℓ. Here we will be interested in what values v_1 takes on in the membrane at its surfaces, i.e. v_{10} and $v_{1\ell}$. The membrane surfaces will be in equilibrium with the liquids they contact. As previous arguments and experiments have shown[14,20], the upstream surface will remain at the equilibrium swelling value, i.e. $v_{10} = v_1^*$. On the other hand, liquid will be squeezed from the downstream surface[14] so $v_{1\ell}$ will be a value less than v_1^*. Fig. 2 illustrates how $v_{1\ell}$ is reduced as $(p_o - p_\ell)$ is increased. Experiments have been made[21] which demonstrate this effect of pressurizing a swollen polymer in equilibrium with a liquid at a lower pressure (through a porous plate).

Now we turn our attention to methods to predict the extent that $v_{1\ell}$ is reduced below v_1^* by pressurization. The dashed line in Fig. 2 represents the linear prediction of models of the LMR type; however, it is clear that such a prediction must break down at some finite pressure since $v_{1\ell}$ must approach zero asymptotically as the pressure is raised indefinitely. A convenient method of analyzing this thermodynamic response is to consider the pressure inside the membrane[9]; however, alternate approaches can be used which avoid this and may be preferred by some if this concept proves troublesome

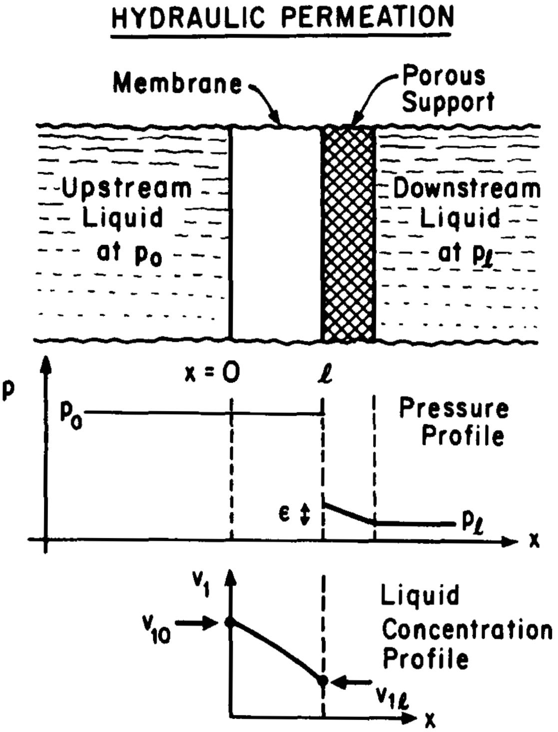

FIGURE 1

Schematic representation of membrane configuration in hydraulic permeation experiment. When the transport mechanism is by solution-diffusion the middle part shows the pressure profile while the lower part shows the liquid or solvent concentration profile in the membrane.

for them. All of the observed responses are consistant with the pressure in the membrane being constant and equal to p_o as shown in the middle diagram of Fig. 1. Mechanical arguments have been given[9,14] to show that this should be the case. Fig. 1 also shows the pressure on the liquid, not the solid support material, in the porous support. Naturally under flow conditions there must be some gradient but for most situations

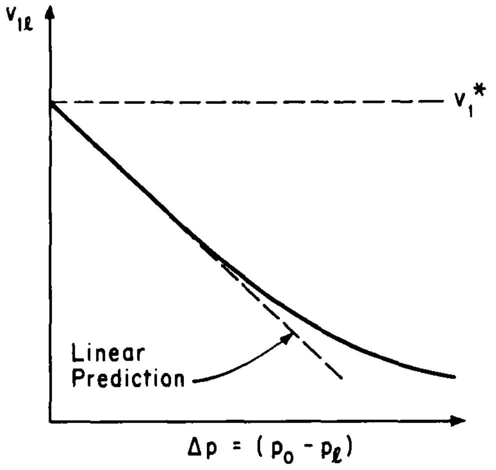

FIGURE 2

Effect of applied pressure on the solvent volume fraction in the membrane at its downstream surface. The dashed line is the linear prediction of LMR-type theories while the solid line is the more general result.

it will be small and we will regard it as zero, i.e. $\varepsilon = 0$ in Fig. 1. There will be a pressure discontinuity or jump at $x = \ell$ which the liquid experiences as it leaves the membrane, and it is this jump which is responsible for the reduction in $v_{1\ell}$ below v_1^* shown in Fig. 2.

By a variety of thermodynamic arguments it is possible to show that the activity of the liquid within the membranes at its downstream surface, $a_{1\ell}^m$, is[7,22,23]

$$a_{1\ell}^m = e^{-V_1(p_o - p_\ell)/RT} \qquad 1$$

if there is pure liquid 1 on both sides of the membrane. These arguments assume that the molar volume, V_1, is equal to the <u>partial</u> molar volume, $\overline{V}_1$, of the liquid in the membrane. As the activity of liquid in the membrane at this surface is reduced by the application of a pressure differential, see eq. 1, the equilibrium liquid content is reduced since by thermodynamics there must be a simple monotonic relation between activity and swelling[15]. To predict a value for $v_{1\ell}$ one needs this latter relation and eq. 1. Data of this type and its use have been described in detail[15].

It is of interest to note that in the solution-diffusion model one uses thermodynamics to obtain the boundary conditions on the membrane, i.e. v_{10} and $v_{1\ell}$ in this case. Once the thermodynamic conditions create a concentration difference between the two membrane faces, diffusion can occur by the resulting concentration gradient. The relation between the diffusion flux and this gradient will be considered later, but before doing so it is of interest to review the experimental evidence for the theoretically predicted gradient since its existance is essential to a solution-diffusion mechanism. Rosenbaum and Cotton[22,23] were the first to report direct observation of this gradient in hydraulic permeation. Their experiments were done using the cellulose acetate-water system. We reported similar observations for a more highly swollen organic system[8]. Our results showed that the details of this liquid concentration profile were in accord with our quantitative predictions which thermodynamically rules out any pressure gradient within the membrane because all of the free energy supplied to the system, $V_1(p_o - p_\ell)$, is totally consumed to create a gradient of this magnitude. Thus we conclude that the concentration profile in the membrane is that given by the lower part of Fig. 1 with $v_{10} = v_1^*$ and $v_{1\ell}$ can be predicted from suitable thermodynamic data with the aid of eq. 1.

Calculation of the Flux From Fick's Law

When the liquid content is small it is adequate to use the following form of Fick's law to compute the volumetric flux of liquid, J_1, through the membrane

$$J_1 = -D\frac{dv_1}{dx} = \frac{D(v_{10} - v_{1\ell})}{\ell} \qquad 2$$

where D is the mutual diffusion coefficient for the membrane-liquid system. This coefficient has been assumed constant in eq. 2. Other kinds of diffusion coefficients than the mutual one can be used and prove useful in certain cases as will be seen later. For more highly swollen systems it is necessary to use more general forms of Fick's law which pay proper attention to frame of reference considerations[11,14]. The form for the present case is

$$J_1 = -\frac{D}{(1-v_1)}\frac{dv_1}{dx} \qquad 3$$

The development and use of this expression for highly swollen systems has been discussed in detail[7-18]. In general D will depend rather significantly on v_1 and integration of eq. 3 is complicated by this fact[15].

Relationship Between Hydraulic Permeation and Pervaporation

For the solution-diffusion mechanism, the liquid flux is determined only by the magnitude of the gradient and should not depend on how the gradient is induced. Application of a hydraulic pressure is only one way this may be done. Pervaporation is another. Fig. 3 outlines the basic features of this latter process in which one has a liquid upstream (pure in this case) and a vapor downstream at a partial pressure, p_1, less than the

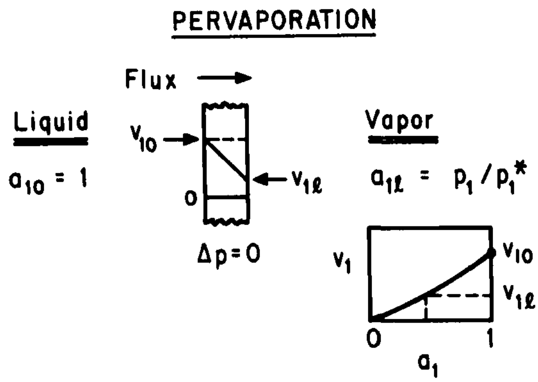

FIGURE 3

Schematic illustration of the pervaporation mode of membrane operation.

equilibrium vapor pressure of the liquid, p_1^*. The reduced activity, given by p_1/p_1^*, results in a value of $v_{1\ell}$ less than v_{10} (which is equal to v_1^* since $a_1 = 1$ upstream) as the schematic diagrams in Fig. 3 suggest. The diagram of v_1 vs. a_1 is the same thermodynamic relation referred to earlier in connection with eq. 1. Thus one could establish the same concentration differential across a membrane, $v_{10} - v_{1\ell}$, by application of a hydraulic pressure upstream or by a vacuum downstream. According to the solution-diffusion model the flux should be the same for either case. Extensive experiments have shown this to be the case[8,15].

This knowledge has important ramifications for membrane processes. First, it is clear that the maximum flux one can obtain occurs when $v_{1\ell} = 0$. This happens in pervaporation when $p_1 = 0$ and in hydraulic permeation when $(p_o - p_\ell) \to \infty$. Thus there is a ceiling flux which cannot be exceeded. Models such as the LMR type which predict flux to be linear in applied pressure assume that one is always far below this flux and of course such models must break down as the flux becomes an appreciable fraction of this value. One can easily measure this flux in a pervaporation experiment where a very good vacuum is maintained on the downstream side. As a practical matter, one can usually expect to achieve higher fluxes in a pervaporation mode than in a hydraulic permeation mode for the same membrane. Also the former will generally produce better separation of mixtures than the latter[17].

SIMPLIFIED MODELS FOR HYDRAULIC PERMEATION AND PERVAPORATION

The previous section outlined the basic principles for modeling solvent transport through membranes. However, the complexities of real systems prevent these concepts from being reduced to simple mathematical relations in many cases. For example, high swelling requires inclusion of frame of reference terms in Fick's law, i.e. the $(1 - v_1)$ factor in eq. 3, while concentration dependent diffusion coefficients require detailed knowledge of this dependency before Fick's law can be integrated and even then complex relations between flux and the differential $(v_{10} - v_{1\ell})$ results. Lack of thermodynamic ideality requires detailed data in addition to v_1^* to characterize the v_1 vs. a_1 relation needed to relate $(v_{10} - v_{1\ell})$ to the external thermodynamic conditions, i.e. $(p_o - p_\ell)$ or p_1/p_1^*. It is instructive to consider a situation, even though it may be only hypothetical, where these complexities do not exist in order to understand the nature of the relation between solvent flux and external factors.

Fig. 4 summarizes such a situation where $v_{10} << 1$, D is constant, and the relation between v_1 and a_1 is linear. From this, it is seen that solvent flux (see equation in box) is related

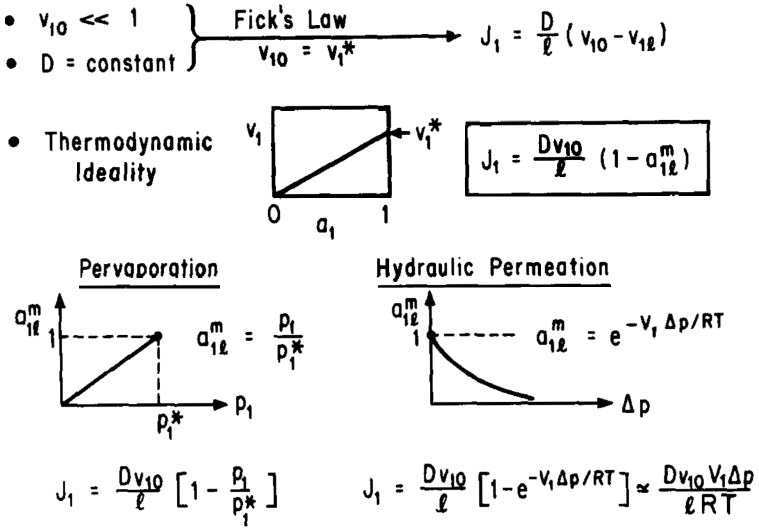

FIGURE 4

Summary of results for the solution-diffusion model for the idealized conditions defined at the top of the figure.

to membrane thickness, the magnitude of D, the degree of equilibrium swelling $v_1^* = v_{10}$, and finally the activity of the solvent in the membrane at its downstream surface. The latter is related to external thermodynamic factors, viz. p_1/p_1^* or $V_1(p_o - p_\ell)/RT$. The relations at the bottom of Fig. 4 show how flux is related to these factors. For hydraulic permeation, the flux is non-linearly related to Δp in general, but for small values of $V_1 \Delta p/RT$ a series expansion of the exponential term retaining only first terms produces a linear relation which is identical with the result from the LMR model[6]. For both modes of operation the maximum or ceiling flux is Dv_{10}/ℓ.

EFFECT OF PRESSURE ON SOLUTE REJECTION IN REVERSE OSMOSIS

Thus far only the transport of solvent has been considered. However, transport of solutes such as salts are an essential consideration in processes like reverse osmosis. Expressions for solute transport rates in terms of the solution-diffusion model can be developed. In most situations the solubility of solute in the membrane is described by a constant distribution coefficient, $K_s = C_s^m / C_s^L$. For simple systems like those in Fig. 4, the solute flux would be given by

$$J_s = \frac{D_s}{\ell}(C_{so}^{m} - C_{s\ell}^{m}) \qquad 4$$

In the development of the LMR model for desalination[6, 24] it was argued correctly that the effect of the applied pressure on the solute concentration in the membrane would be very small for solutes with small molar volumes, V_s, and highly rejecting membranes so eq. 4 may be replaced by

$$J_s = \frac{D_s K_s}{\ell}(C_{so}^{L} - C_{s\ell}^{L}) \qquad 5$$

where C_{so}^{L} and $C_{s\ell}^{L}$ refer to solute concentration in the liquid phases upstream and downstream of the membrane respectively.

Solute rejection defined as

$$R \equiv 1 - \frac{C_{s\ell}^{L}}{C_{so}^{L}} \qquad 6$$

can be written as follows for the LMR model[6]

$$1 - R = \cfrac{1}{1 + \cfrac{K_o(\Delta p - \Delta\pi)}{D_s K_s}} \qquad 7$$

where $\Delta\pi$ is the osmotic pressure differential across the membrane, and K_o is the initial (low pressure limiting) hydraulic permeability defined by $J_1 = K_o \left(\frac{\Delta p - \Delta\pi}{\ell}\right)$ which in the LMR model is given by

$$K_o = \frac{D v_{10} V_1}{RT} \qquad 8$$

In the case of low solute rejections (when $\Delta\pi$ would be essentially zero) and/or when solute molar volume is not small, the effect of pressure on solute flux and rejection may not be negligible. Lonsdale, Merten, and Tagami[25] considered this effect in a study where phenol was the solute because of its rather high molar volume and low rejection by cellulose acetate membranes. Their analysis followed the spirit of the earlier LMR development that led to eq. 7. As a result the Δp effect on salt flux appeared as a linear term in the replacement for eq. 7 (with $\Delta\pi = 0$) given below

$$1 - R = \cfrac{1 + V_s \Delta p/RT}{1 + \cfrac{K_o \Delta p}{D_s K_s}} \qquad 9$$

Our purpose for this discussion is to show how this effect would enter the more general formulation which does not assume the simpler linear behavior. This development follows.

The general form of eq. 1 for any component, i, where there are mixtures upstream and downstream of the membrane is as follows[7]

$$\text{at} \quad x = 0 \qquad a_{io}^{m} = a_{io}^{L} \tag{10}$$

$$\text{at} \quad x = \ell \qquad a_{i\ell}^{m} = a_{i\ell}^{L}\, e^{-V_i(p_o - p_\ell)/RT} \tag{11}$$

If we apply these equations to solute, let i = s, and assume that thermodynamic ideality exists so that concentrations are proportional to activity in both phases, we can obtain the following from equations 10 and 11

$$C_{so}^{m} = K_s C_{so}^{L} \tag{12}$$

$$C_{s\ell}^{m} = K_s C_{s\ell}^{L}\ e^{-V_s(p_o - p_\ell)/RT} \tag{13}$$

These results combined with eq. 4 give

$$J_s = \frac{D_s K_s}{\ell}\left[C_{so}^{L} - C_{s\ell}^{L}\, e^{-V_s\,\Delta p/RT}\right] \tag{14}$$

The rejection then becomes (for $\Delta\pi = 0$)

$$1 - R = \frac{1}{e^{-V_s\Delta p/RT} + \dfrac{K_o\Delta p}{D_s K_s}} \tag{15}$$

In the limit of small values of $V_s\,\Delta p/RT$ the exponential in eq. 15 can be expanded in a series and truncated. The result can be shown to be mathematically equivalent to eq. 9. That is, the modified LMR result is just the limiting linear form of eq. 15. Eq. 15 has never been tested against experimental data but should be regarded as superior to eq. 9 for large values of $V_s\,\Delta p/RT$. It is interesting to note that eq. 7 (which does not consider the effect of Δp on solute) predicts that the solute rejection can never be less than zero (negative). Both eq. 9 and 15 would predict negative rejections under certain conditions. Negative rejections have been observed[25], but it is not clear that the sole reason for this is the effect of pressure on the solute.

A SCHEME FOR PREDICTING HYDRAULIC PERMEABILITY

The hydraulic permeability is an important parameter for many applications, and it would be quite useful to be able to estimate it by some approximate technique. It is the purpose here to present such a procedure. In previous papers[13,18], we showed that the hydraulic permeability in general is given by

$$K_o = \frac{v_{10} V_1}{(1 - v_{10}) RT} D_1(v_{10}) \qquad 16$$

where D_1 is the "thermodynamic" diffusion coefficient for the liquid in the membrane. It will depend on the level of swelling v_{10}. This diffusion coefficient is related to the mutual diffusion coefficient, D, in eq. 3 by a thermodynamic factor and in many cases it will be very nearly equal to the diffusion coefficient one would obtain for the liquid in the membrane by a radioactive tracer technique[13,18]. Note that the term $(1 - v_{10})$ in eq. 16 stems from the $(1 - v_1)$ term in eq. 3. It does not appear in eq. 8 because there we assumed $v_{10} << 1$ (note that in this limit $D_1 = D$). Many references in the literature do not include this term even in cases when it should be included[13].

In view of the above, all we need in order to calculate K_o is v_{10} and a way to estimate D_1. Fig. 5 proposes a way to do the latter. In this figure we have plotted several things but first we will examine the dotted and dashed curves. The upper dashed curve is a plot of experimental tracer diffusion coefficients for

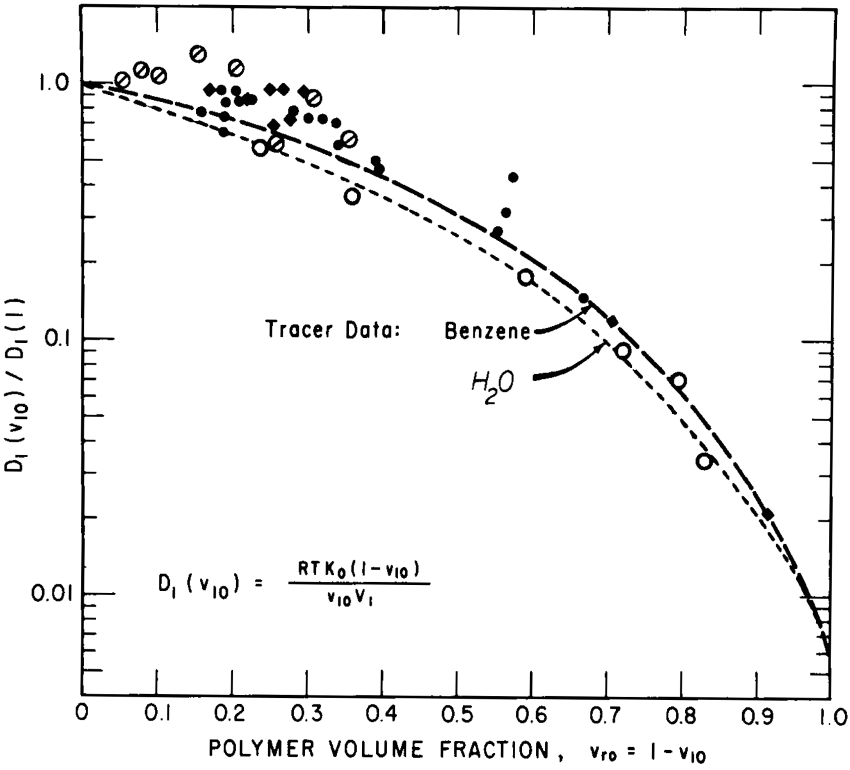

FIGURE 5

Scheme for estimating the hydraulic permeability of a membrane. See text for meaning of symbols.

benzene in a organic rubber over the entire range of v_{10}[26] normalized by the tracer diffusion coefficient for pure benzene, $D_1(v_1 = 1)$. The lower dotted curve is similar data for water in a series of methacrylate hydrogels reported by Yasuda, Lamaze, and Peterlin[27]. It is quite interesting that the tracer data (normalized by the self-diffusion coefficient for the given liquid, $D_1(1)$) are about the same regardless of the liquid or polymer type. We suggest that this might be a good approximation for most systems. This will allow us to estimate $D_1(v_{10})$ for any system if we measure v_{10} and determine $D_1(1)$ from the literature (the value for H_2O at $25^\circ C$ is $\sim 2.8 \times 10^{-5}$ cm^2/sec) or estimate it by suitable techniques[18]. The procedure to follow is: locate on Fig. 5 the abscissa dictated by v_{10}, read off a value $D_1(v_{10})/D_1(1)$ defined by the dotted or dashed curves (an average would be recommended), multiply by $D_1(1)$ and insert into eq. 16 to get K_o.

How well does this work? We have tested this scheme for a variety of systems, and the various points on the graph show the comparison. From measured values of K_o, we computed $D_1(v_{10})$ using eq. 16. This value was normalized by $D_1(1)$ and plotted at the appropriate v_{10} in Fig. 5. The small solid points are data for a wide range of organic liquids in rubbery polymers[18]. The large circles with a slash are the permeability data of White[28] for water in polyacrylamide gels. The large open circles are data by Riley, Lyons and Merten[29] for water in a series of polyvinylpyrrolidone-polyisocyanate membranes (results from their Figures 1 and 3). In general, the points fall about the dotted and dashed curves very closely - probably within the accuracy of some of the measurements. Thus we conclude that this would be an adequate method to obtain an initial estimate of K_o from very little information. The limits of applicability of this scheme have not been explored further than what is shown here.

SUMMARY

The relations and conclusions discussed here are strictly limited to those cases where transport indeed does occur by a solution-diffusion mechanism, and it should be understood that other membrane mechanisms exist and can be operative in many important cases. Sometimes determination of the actual mechanism is not easy or obvious. The treatment of solution-diffusion mechanisms given here is more general than the LMR results developed earlier which only apply for slightly swollen systems and for small values of $V_i \Delta p/RT$. The present results are not the most general ones possible and still may not incorporate effects that could prove important in some cases.

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