Use of a Gee Relationship in a Diffusion Study

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Synopsis

Paul and Ebra-Lima[6] reported on the pressure-induced transport of 12 organic liquids through a highly swollen rubber membrane. Gee[10] examined the capability of a liquid to swell a rubber and the interaction between liquid and rubber from the standpoint of the Hildebrand-Scatchard solubility parameter. In this presentation, the swelling function of Gee was expressed by $[V_0(\delta_0 - \delta_r)^2(1 - v_0)^2]^{1/2}$ where V and δ are the molar volume and solubility parameter of the liquid 0 and the rubber r and $(1 - v_0)$ represents the volume fraction of rubber when the rubber is fully swollen by that liquid. The data of Paul and Ebra-Lima are analyzed in terms of the swelling function. It is principally assumed that the flux is a function of the swelling power of the liquid. The analysis indicates that the use of the Gee relationship provides values for the energetics of the various steps in the transport process and a means for differentiating between various types of penetrant liquids.

INTRODUCTION

Common underlying principles and mechanisms are used[1-6] to explain the separation of gases and liquids on the basis of transport through a polymeric membrane. The mechanism of a permeation process is generally considered to involve three consecutive steps: solution or absorption of the permeating molecule at one surface of the membrane, activated diffusion of the penetrant molecule through the membrane, and desorption from the membrane surface. For the case of the so-called permanent gases, it has been demonstrated that their solubility obeys Henry's law and the diffusion obeys Fick's laws. This may be ascribed[1] to the absence of polymer–penetrant interactions in these systems. For the case of liquids, the solubility and/or diffusivity have been related to various polymer–penetrant interactions. Sweeny and Rose[2] studied the separation of organic mixtures using polymer films. They concluded that hydrogen bonding played an important role in the separation process. In addition, they found that the component whose polarity most closely matched that of the membrane was preferentially permeated; polar compounds tended to permeate polar membranes faster than nonpolar compounds, and vice versa. Huang and Lin[3] and Michaels et al.[4] came to the same conclusion. Huang and Lin[3] found that liquids with solubility parameter δ close to that of the polymer sorb to a greater extent and permeate faster than solvents which have values of δ that are far from that of the polymer. Michaels et al.[4] found

that liquid flux rates through polypropylene films depend primarily upon the solubility of the permeants in the films and that the absolute difference of the solubility parameter of the polymer–liquid pair reflected a good correlation of this effect.

Structural and hydrodynamic factors have been used in discussing the efficiency of polymer membranes in separating liquid mixtures. Huang et al.[3,5] studied the effect of molecular size and shape on the permeation through PE film[3] and through cellophane and poly(vinyl alcohol) membranes.[5] They explained their results on the basis of an "internal plasticizing effect" arising from the molecular volume as well as the maximum molecular length of the permeating liquid. For molecules with similar shape and chemical nature, the permeation rate was found to decrease with increasing molecular length of the permeating liquid. Michaels et al.[4] reported that for liquids of closely similar solubility parameter, fluxes depended upon the apparent molecular cross sections of the permeants. Paul and Ebra-Lima[6] studied the pressure induced diffusion of 12 organic liquids through a highly swollen rubbery membrane. They found that, although the flux was a highly nonlinear function of the driving pressure, a correlation existed between the membrane–solvent diffusion coefficient and the fluidity of the solvent.

The basis of a membrane separation process is the selective permeation of the permeating molecule through the membrane. Membrane selectivity is affected by polymer morphology. Michaels et al.[7,8] present a model based on the polymer acting as a molecular sieve or screen, wherein the amorphous region constituted the holes and the interconnecting crystalline regions constituted the mesh. Huang and Lin[3] report that the degree of crystallinity and size of the crystallites within the polymer affect both the transport and the efficiency of separation. Since only amorphous regions in the polymer take part in the transport process, in highly crystalline polymers any factor which disrupts the order of these regions can have an effect on the liquid permeation process. Preconditioning of the membrane may affect the permeation process. Swelling affords a loosening of the polymer structure allowing the polymer segments to move more freely about the polymer backbone. As the amorphous portion of the polymer swells, a greater proportion of the total polymer becomes available for diffusion. Thus, an increase in the swelling agent concentration or capability may be expected to increase the diffusion rate.

As noted, the permeation and flux rates of organic liquids through polymer films have been related either to the difference in solubility parameter of the liquid and membrane or to the molecular dimensions of the penetrant. Although the swelling of the membrane by the liquid is recognized as being a factor in the diffusion process, its effect is treated more or less qualitatively, if at all.

No studies are known that examine the transport process from the three aspects of liquid molar volume, liquid swelling capability, and interaction between the liquid and membrane. In a recent article, though, Laine and

Osburn[9] correlated permeation of organic vapors through polyethylene film to two of these components, namely, molar volume of the liquid, and the interaction between film and liquid as represented by the difference in solubility parameters. In order to study the transport process in terms of the "chemical" aspects of molar volume, penetrant–membrane interaction and swelling capability of the liquid, the data of Paul and Ebra-Lima[6] are analyzed using a relationship suggested by Gee.

Gee[14] has shown that the degree of swelling of vulcanized rubber by various liquids is related to the heats of mixing which, in turn, are related to the difference between the cohesive energy densities of the liquid and rubber, as in equation (1):

$$\Delta H_0 = kV_0[(E_0/V_0)^{1/2} - (E_1/V_1)^{1/2}]^2(1 - v_0)^2 \tag{1}$$

where ΔH_0 is the partial molar heat of dilution; V_0, V_1, E_0/V_0, E_1/V_1 are the molar volumes and molar cohesive energy densities of the liquid and rubber, respectively; v_0 is the volume fraction of the liquid when the rubber is fully swollen by that liquid; and k is an adjustable parameter but must be close to unity. Gee's relationship consists of three parts: (1) the molar volume of the liquid, which is related to the molecular dimensions of the penetrant; (2) the difference in the solubility parameters between the penetrant and the membrane; and (3) the term $(1 - v_0)$ which represents the volume fraction of rubber present when the rubber is fully swollen by that liquid. Since, in the instance of Paul and Ebra-Lima's studies, we are dealing with a single liquid and a single membrane, the term $(1 - v_0)$ is taken to represent the capability of the liquid to swell the rubber membrane.

In this report, the data of Paul and Ebra-Lima on the transport of liquids through a highly swollen rubber membrane were analyzed in terms of the Gee relationship as given by eq. (1). It is recognized that entropy needs to be considered when accounting for the swelling behavior of rubber by various liquids. The approach of Gee was followed in assuming that the partial molar entropy ΔS_0 was small and that for a range of liquids, differences in ΔS_0 may be small. Since the studies of Paul and Ebra-Lima[6] were conducted at constant temperature, 30°C, the effect of assuming that ΔS_0 is the same for all liquids is to tacitly hope that the change in free energy is proportional to the heat of mixing of the liquid with the rubber.

The analysis was based on the primary assumption that the steady-state flux is a function of the swelling capability, Q, of the liquid. It was further assumed that, since the rubber is essentially nonpolar, polymer–liquid interactions are slight; interactions such as hydrogen bonding, dipole–dipole effects are not important in this case so that only the nonpolar components of the solubility parameter can be used. In this study, the parameter k, eq. (1), was set equal to unity, and the following relationship was used:

$$f(Q) = \Delta H_0 = [V_0(\delta_0 - \delta_r)^2(1 - v_0)^2]^{1/2} \tag{2}$$

where δ is the solubility parameter and the subscripts 0 and r refer to liquid and rubber, respectively. Bearing in mind that, in each case, we are deal-

ing with a single rubber and liquid, the term $(1 - v_0)$ represents the volume fraction of swollen rubber. Thus, $(1 - v_{l0})$ and $(1 - v_{l0})$ describe, respectively, the volume fraction of rubber when the rubber is fully swollen by that liquid as it is placed in the apparatus prior to pressurization and, after pressurization, at the upper surface of the membrane. Substitution into eq. (2) provides eq. (3),

$$f(Q) = \Delta H_0 = [V_0(\delta_0 - \delta_r)^2(1 - v_{l0})^2]^{1/2} \qquad (3)$$

which can be taken to represent the potential energy of the system available for absorption, diffusion, and desorption. Paul and Ebra-Lima provided a value, v_{r0}, for the volume fraction of rubber in the fully swollen state as it is installed in the apparatus. The relationship $(1 - v_{r0}) = v_{l0}$ was used. It is reasonable to correlate the part of the energy assigned to absorption to the interaction parameter between polymer and liquid, as given by eq. (4):

$$\chi_H = [V_0(\delta_0 - \delta_r)^2(1 - v_{l0})^2]^{1/2}. \qquad (4)$$

Paul and Ebra-Lima determined the parameter χ_l for each liquid–membrane pair. A value of 0.34 was deducted for the entropy contribution[11,12] in nonpolar systems to provide the parameter χ_H. The volume fractions of liquid at the upper surface of the membrane, v_{l0}, and at the lower surface, v_{1l}, were calculated as follows: From Figures 7–10, their manuscript, values for $(v_{l0} - v_{1l})$ were picked off at a flux rate of 2 cm³/cm² day. (The assumption was made that the process is diffusion controlled at this flux rate. This appears reasonable from an energy viewpoint. For example, for benzene, a flux rate of 9.65 cm³/cm² day was obtained at a pressure differential of 400 psi.) Use was then made of eq. (27), their manuscript (shown as eq. (5) below), which they used to develop their diffusion theory and which relates the steady-state flux to the difference in volume fractions of liquid found at the two surfaces of the membrane:

$$n_1 V_1 = \frac{D}{l_d v_{r0}^{2/3}} (v_{l0} - v_{1l}) \qquad (5)$$

where D is the diffusion coefficient and l_d is the thickness of the dry membrane. Since the flux rate was taken at a constant value, 2 cm³/cm² day, and the thickness of the dry membrane was constant, the "effective" volume fraction of rubber at the upper surface, after pressurization, was taken as $v_{r0}^{2/3}$. The volume fraction of liquid at the upper surface of the membrane v_{l0} was taken as being equal to $(1 - v_{r0}^{2/3})$. A value of v_{1l} then followed directly.

Laine and Osburn[9] consider that the Hildebrand solubility parameter is associated with the energy necessary to force the molecule through the surrounding structure and that it should be related to the energy of permeation. Bearing in mind that in eq. (5), $n_1 V_1$, l_d, and $v_{r0}^{2/3}$ for a given liquid are constant and that the energy for diffusion of the liquid through the swollen membrane is related to the volume fraction of liquid found at the

two surfaces, and using the primary assumption that the steady-state flux is a function of the swelling capacity of the liquid, eq. (6) is obtained:

$$1/D \sim \{[V_0(\delta_0 - \delta_r)^2]\}\{[(1 - v_{10})^2]^{1/2} - [(1 - v_{1l})^2]^{1/2}\} \qquad (6)$$

where $(1 - v_{1l})$ represents the volume fraction of swollen rubber at the lower surface of the membrane, after pressurization. The value on the right-hand side of the proportionality sign turned out to be negative. This is in line with the finding[14] of Paul and Ebra-Lima that the volume fraction of liquid in the membrane at the downstream surface is reduced by the action of the applied pressure.

In order to evaluate the energy available for desorption, the system was considered to be closed. Then, the difference between the potential energy of the system, obtained by use of eq. (3), and the sum of that ascribed to absorption, eq. (4), and diffusion, eq. (6), was set equal to zero.

DISCUSSION

Table I shows the summary of the pertinent experimental data at 30°C taken from Paul and Ebra-Lima.[6] For convenience, the solubility parameter δ_0 of the liquids was added; values for δ_0 were available at 25°C[13] and were used without further correction. A plot was prepared of $[1/V_0(1 - v_0)^2]^{1/2}$ versus δ_0; values of V_0 and $(1 - v_0) = v_{r0}$ were taken from Table I. The results indicated that a maximum value of δ occurs at 8.58, which was taken as the solubility parameter of the rubber membrane used in this study.

TABLE I
Summary of Pertinent Experimental Results at 30°C[a]

Liquid	V_0, cc/mole	v_{r0}	χ_l	$v_{10} - v_{1l}$[b]	$D \times 10^6$, cm²/sec	n_1V_1,[c] cm³/ cm² day	δ_0,[d] (cal/ cc)$^{1/2}$
Benzene	88.9	0.207	0.474	0.076	2.37	3.71	9.16
Toluene	106.0	0.190	0.425	0.074	2.36	3.94	8.93
o-Xylene	118.4	0.187	0.408	0.096	1.78	3.06	9.06
Tetralin	136.0	0.185	0.371	0.203	0.82	2.30	9.50
n-Hexane	130.8	0.337	0.587	0.062	4.06	4.04	7.27
n-Heptane	146.0	0.301	0.541	0.072	3.07	3.68	7.50
Isooctane	165.1	0.339	0.572	0.136	2.73	2.02	7.34
Cyclohexane	108.0	0.205	0.448	0.102	1.80	2.76	8.19
Cyclohexanone	98.4	0.281	0.551	0.353	0.66	1.18	10.42
MEK	89.1	0.619	0.891	0.085	4.09	0.75	9.45
MIBK	125.2	0.394	0.643	0.177	1.67	1.10	8.57
CCl₄	96.5	0.161	0.353	0.097	1.67	2.79	8.55

[a] Data taken from ref. 6.

[b] Values for the difference in volume fractions of liquid found at the upper and lower surfaces of the rubber membrane, v_{10} and v_{1l}, respectively, were taken from Figures 7–10, at a flux rate of 2 cm³/cm² day, ref. 6.

[c] Volumetric flux at 100 psi was calculated by use of eq. (28) of ref. 6.[14]
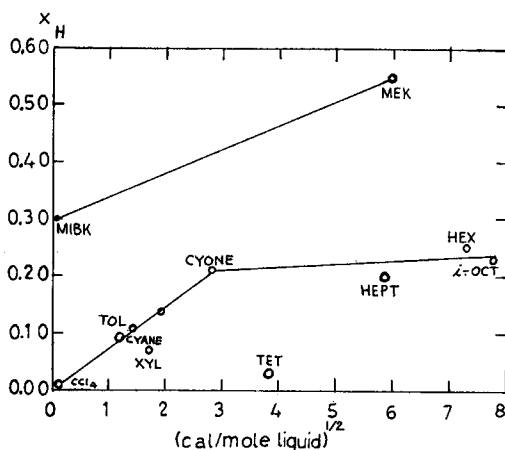
[d] Data at 25°C taken from ref. 13.

Fig. 1. Plot of χ_H vs. $[V_0(\delta_0 - \delta_r)(1 - v_{10})^2]^{1/2}$; values for χ_H were obtained by subtracting 0.34 from the experimentally determined χ_l values give in ref. 6. Calculated values for the swelling function are given in Table II under column B.

The energies ascribed to liquid absorption, eq. (4), and diffusion, eq. (6), were related to the experimental results. The data presented in Figure 1 show that the hydrocarbons, CCl₄, and cyclohexanone are characterized by χ_H values equal to or less than 0.25. Except for tetralin, the energy required for absorption increases with increasing values of χ_H. Significantly less energy, less than 2 (cal/mole liquid)$^{1/2}$, is required for absorption of liquids exhibiting χ_H values of less than 0.15 as compared to liquids with values greater than 0.15, more than 5.8 (cal/mole liquid)$^{1/2}$. The effect of the ketone moiety in cyclohexanone is apparently minimal, falling in with the general class of aliphatic liquids. On the other hand, the two ketones, MIBK and MEK, characterized by $\chi_H \geq 0.30$, fall into a separate class. In this instance, too, the volume fraction of liquid found at the upper surface of the membrane, v_{10} (Table II), is much less for these two ketones, 0.462 and 0.274, as compared to the rest of the liquids, 0.513 to 0.704 cc liquid/cc rubber.

The energy ascribed to diffusion was calculated (Table II), multiplied by minus one, and plotted as shown in Figure 2. The results show that the liquids used in this study fall into three separate groups, one group comprising MIBK and CCl₄, another comprising liquids with χ_H values of less than 0.15 and a third comprising values greater than 0.20. For the first group, the solubility parameter of the liquid is close to that of the membrane (Table I), the values calculated using eq. (6) are close to zero, and the diffusivity through the membrane is high. From Figure 1, for these two liquids, the amount of energy expended for absorption is much smaller also, approximately one-tenth of that expended by the other liquids. Apparently, the liquids are very weakly absorbed or interact very weakly with the membrane, and the heats of absorption are sufficient for diffusion. For the latter two classes of liquids, diffusivity increases with increasing ex-

TABLE II
Summary of Calculated Results[a]

Liquid	v_{10}	A	B	C	D
Benzene	0.650	1.129	1.914	−0.354	−0.431
Toluene	0.670	0.684	1.187	−0.268	−0.235
o-Xylene	0.673	0.976	1.705	−0.500	−0.229
Tetralin	0.675	1.985	3.810	−2.38	+0.555
n-Hexane	0.514	4.390	7.28	−0.93	−1.96
n-Heptane	0.551	3.92	5.85	−0.99	−0.94
Isooctane	0.513	5.15	7.76	−1.17	−1.44
Cyclohexane	0.652	0.832	1.410	−0.414	−0.164
Cyclohexanone	0.571	5.13	2.82	−6.45	+3.76
MEK	0.274	5.08	5.96	−0.70	−0.18
MIBK	0.462	0.04	0.0556	−0.0184	−0.0028
CCl$_4$	0.704	0.0475	0.1168	−0.0288	−0.0405

[a] $A \equiv [V_0(\delta_0 - \delta_r)^2(1 - v_{10})^2]^{1/2}$; $B \equiv [V_0(\delta_0 - \delta_r)^2(1 - v_{10})^2]^{1/2}$; $C \equiv \{[V_0(\delta_0 - \delta_r)^2]\}-\{[(1 - v_{10})^2]^{1/2} - [(1 - v_{11})^2]^{1/2}\}$; $D \equiv A - (B + C)$.

penditure of energy (more negative values), but at different rates. Using as a criterion a diffusion rate of 2.0×10^{-6} cm^2/sec ($1/D = 0.5$), for liquids with smaller χ_H values, 0.3 (cal/mole liquid)$^{1/2}$ is expended as compared to 1.9 (cal/mole liquid)$^{1/2}$ for liquids characterized by $\chi_H \geq 0.20$.

The data presented in Figures 1 and 2 indicate that the energetics of absorption and diffusion are interrelated. The parameter χ_H is low for liquids with greater swelling power, $v_{r0} \leq 0.2$, and is high for liquids which do not dissolve the polymer. Preliminarily, the liquids with greater swelling power, χ_H less than 0.15, can be considered as being weakly absorbed. From Figure 1, 1.5 (cal/mole liquid)$^{1/2}$ may be taken as a figure of merit for these liquids as compared to 6 (cal/mole liquid)$^{1/2}$ for heptane as a liquid representative of the second class. The data in Figure 2 show that, at an
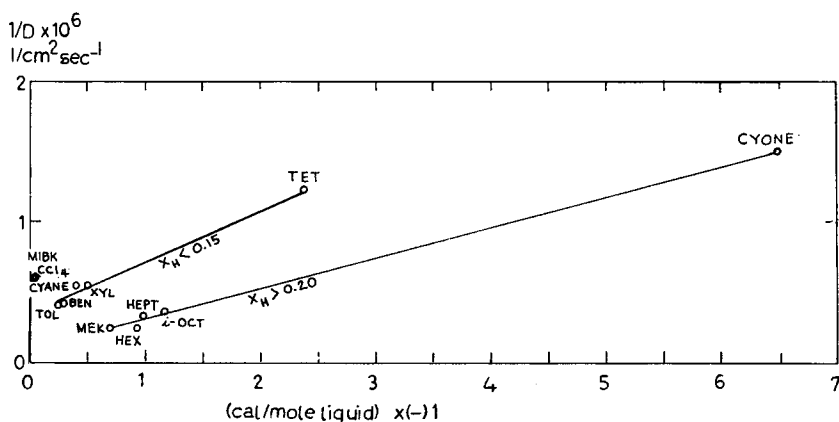

Fig. 2. Plot of diffusivity vs. $\{[V_0(\delta_0 - \delta_r)^2]\}\{[(1 - v_{10})^2]^{1/2} - [1 - v_{11})^2]^{1/2}\}$. Values for $1/D$ were taken from ref. 6. Calculated values for the swelling function are given in Table II under column C.
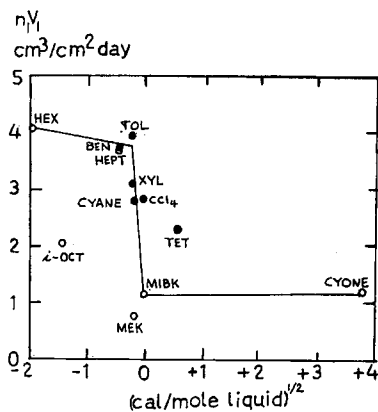
Fig. 3. Volumetric flux vs. residual energy. Values for volumetric flux at a pressure differential of 100 psi were calculated using eq. (28), ref. 6. Calculated values for the residual energy are given in Table II under column D. Darkened circles represent liquids with $\chi_H < 0.15$.

expenditure of 1 (cal/mole liquid)$^{1/2}$, the diffusion rate for heptane is 3×10^{-6} as compared to 1.2×10^{-6} cm^2/sec for the liquids in the weakly absorbed class.

Figure 3 shows the residual energy available for desorption as a function of the flux at a pressure differential of 100 psi. In this graph, the liquids with χ_H values equal to or less than 0.15 are shown as filled circles. The results show some scatter but suggest that a high flux rate may be associated with higher residual energy, i.e., more negative values indicating that less energy is expended in the absorption and diffusion steps. The data also indicate that, for the weakly absorbed liquids, the amount of residual energy does not vary greatly.

Figure 4 shows the correlation between flux and type of liquid. In this figure, the volumetric flux at a pressure differential of 400 psi was used although the same correlation was obtained when data obtained at 100 psi were used. The liquid–membrane interaction parameter, χ_H, was used to differentiate between liquid types. The results clearly point out the effect of chemical moiety on flux and liquid–membrane interaction parameter. The data fall into separate and distinct categories. Tetralin (1,2,3,4-tetrahydronaphthalene) forms the apex of two curves. The first leg consists of the aromatic hydrocarbon derivatives of tetralin, while the second leg consists of the cyclo- and normal-aliphatic derivatives. For the aromatic derivatives of tetralin, flux increases with increasing values of χ_H and decreasing degree of substitution in the aromatic ring; for the aliphatic derivatives (cyclohexane, n-heptane, and n-hexane), flux rate also increases with increasing values of χ_H and with "normalization" of the chain. The chlorinated hydrocarbon, CCl$_4$, and the substituted aliphatic hydrocarbon, isooctane, are in separate classes. As can be seen, the three ketones fall into one, but separate, category, and their flux changes only slightly with
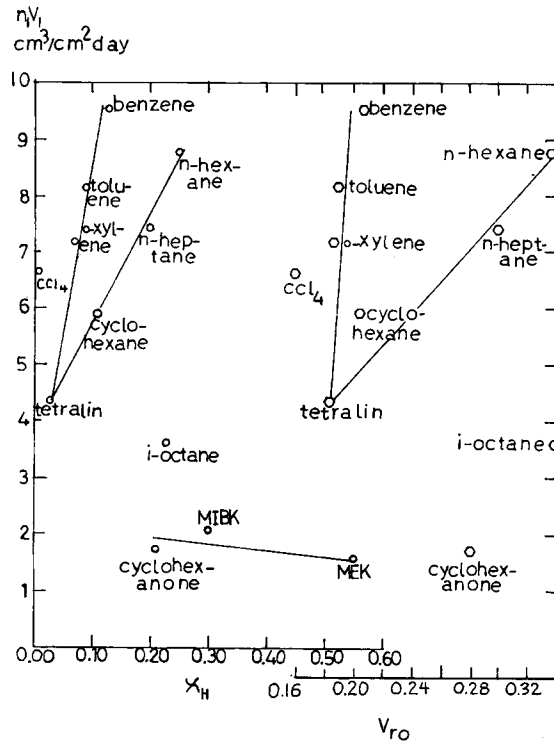
Fig. 4. Correlation between volumetric flux at a pressure differential of 400 psi and chemical moiety: (O) χ_H; (O) v_{ro}. Values for volumetric flux were calculated using eq. (28), ref. 6; χ_H was obtained by subtracting 0.34 from the χ_l values given in ref. 6; for v_{ro}, data were taken from ref. 6.

χ_H values. In addition, a plot of volumetric flux versus the volume fraction of rubber in the fully swollen state, v_{ro}, was similar. A part of this curve is also shown in Figure 4. This is taken as an indication of the validity of the primary assumption that the flux is a function of the swelling capacity of the liquid. Finally, a plot of flux versus molar volume of the liquid did not provide any meaningful relationship.

In summary, the results show that the use of the Gee relationship provides a means for evaluating the contribution of the chemical components in the transport process. The relationship provides values of the energy for the absorption, diffusion, and desorption steps which, based on the limited data available, appear to differentiate between different types of penetrant liquids. The data are too limited to test the various assumptions made in the development of the analysis. However, the consistency of the results of the analysis with the experimental data indicates the basic validity of the use of the Gee relationship in the transport process. It is believed the approach might be useful in establishing mechanisms relating the solubility and transport in membranes with the molecular properties and characteristics of the components.

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