

Sorption and Diffusion in Asymmetric Membranes

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Synopsis

Polyethylene membranes with nearly linear gradients of grafted poly(vinyl acetate) from one surface to the other have been prepared by radiation-initiated polymerization of sorbed vinyl acetate monomer. Transport of methanol through the modified membrane proceeds at different rates, depending on the direction of flow relative to the gradient of grafted PVAc. A mathematical model has been derived, which gives a quantitative description of the directional transport process. The relationship can be used to predict the transport behavior for single penetrants through asymmetric membranes from knowledge of the properties of the individual components.

INTRODUCTION

At present the understanding of the underlying physics and chemistry of membrane permeation is sufficient to make a rational selection of polymeric materials and membrane preparation procedures suitable for most desired uses. The ability to modify a membrane to fit a set of required properties is an ultimate aim of membrane technology. In this work we were specifically concerned with membranes showing a directional preference to flow of a penetrant, a property that would make such membranes very useful in separation processes.

The transmission of a penetrant through a polymer film is a result of a chemical potential (concentration, vapor pressure) gradient. This can be represented by the set of equations¹

$$J_i = \sum_j -L_{ij} (\partial\mu_j/\partial x) \quad (1)$$

where J_i is the flow in the x direction of component i of the system, L_{ij} are the Onsager coefficients, and μ_j is the chemical potential of component j . The chemical potential is a function of, among other variables, the pressure, concentration, and temperature. For simplicity the following treatment is restricted to the isothermal case, note being taken that the incorporation of a temperature gradient will require but a simple extension of the suggested procedure. Thus, in the following the chemical potential is dependent on the pressure and concentration only. The treatment is also time-independent; i.e., a steady state of flux is reached in all cases.

The set of equations (1) affords a mathematical description of a flow system that is not far from equilibrium; however, the mathematical and

experimental complexity of a ternary or higher system makes it excessively inconvenient to resort to this type of treatment, and modified models which are or are not a simplification of equations (1) are more commonly used.

The process of transmission of vapors and gases through a polymer membrane usually is considered to occur in the following way: The penetrant molecules dissolve into the polymer matrix, move across the membrane by an activated diffusion mechanism under a concentration gradient, and then evaporate from the other face of the membrane.

This description is satisfactory, at least qualitatively, for cases in which the chemical potential gradient and the concentration gradient are of the same direction and sign. However, as mentioned before, the chemical potential may be a function of, not only concentration, but also other factors, such as pressure and position in the case of permeation. Under certain conditions these factors may cause the gradient of chemical potential and that of concentration to be in opposite directions and signs. The flow in such case, as always, is along the chemical potential gradient but *against* the concentration gradient. This phenomenon has been observed, especially in biological membranes,^{2,3} and is termed "uphill diffusion." If the simplified Fick's law expression,

$$J = -D (dc/dx) \quad (2)$$

is used to describe the flow in such a case, the diffusion coefficient D will have to be negative, since the concentration gradient is positive under these conditions (i.e., concentration direction is "uphill"). This anomaly is not encountered when the more rigorous expression for flux in terms of chemical potential gradients is used.

The solubility coefficient of a given penetrant in a homogeneous polymer membrane, which is above its glass transition temperature, is not expected to be explicitly position-dependent. Instead, this coefficient is vapor-pressure-dependent or concentration-dependent; thus, it is an implicit function of position in the case of permeation experiments, in which the concentration or relative vapor pressure across the membrane is a function of position:

$$S = S(p) \neq S(x) \quad (3)$$

while

$$p = p(x) \quad (4)$$

where S = solubility coefficient, p = "internal" vapor pressure of penetrant, and x = spatial coordinate. Thus, S is an implicit function of x . However, if the membrane can be so modified as to possess solubility characteristics which are explicitly position-dependent, it can be shown^{4,5} that such a membrane can exhibit the uphill-diffusion phenomenon. Such a membrane will be expected to exhibit a directional preference to the permeation of the soluble penetrant;^{4,5} i.e., under the same experimental

conditions, such as pressure, concentrations, and temperature, the permeation rate of the penetrant through such a membrane in one direction will be faster than in the opposite direction. This is due to the fact that a fixed (with respect to thickness coordinate and time) gradient of solubility has been superimposed on all other gradients, which adds to the flow in one direction while opposing it in the reverse direction. For such a membrane

$$S = S(p, x) \quad (5)$$

$$dS/dx = (\partial S/\partial p) (dp/dx) + (\partial S/\partial x)$$

where $(\partial S/\partial x)$ is the permanent solubility gradient, which adds to, or subtracts from, the total solubility gradient dS/dx , depending on the relative directions of the fixed solubility gradient and the flow.

Consequently, if a membrane possessing a fixed internal chemical potential gradient is available, the directional preference phenomenon should be observed. Numerous methods for the preparation of such membranes^{4,5,7} have been suggested, and the effect has been shown to exist in the case of polymer laminates⁵ and polymer membranes with a fixed internal gradient of composition.⁴

In this investigation an effort is made to account quantitatively for the different permeation fluxes in asymmetric membranes. For this purpose exact quantitative analysis of the membrane spatial composition is essential. Polymer membranes with a fixed, chemical composition gradient from one surface to the other surface have been prepared by radiation-initiated polymerization of sorbed monomer. Details of the method of preparation and characterization of such membranes are described elsewhere.⁸ The membrane used for this study was a polyethylene ($\rho = 0.92$ g./ml.) film possessing a very nearly linear gradient of grafted poly(vinyl acetate) from the PVAc-rich face of 9% by volume to the face of nil-grafted polymer. The linear quality of the gradient in this experiment does not detract from the general applicability, for any shape of gradient, of the procedure adopted.

EXPERIMENTAL

A copolymer membrane of polyethylene (density 0.92 g./ml.) and poly(vinyl acetate) possessing a linear gradient of composition, from face to face, was prepared by polymerizing a sorbed monomer (vinyl acetate) in a pure polyethylene (PE) film by radiation initiation. The radiation source was a Van de Graeff electron generator operated to give 6 M.e.v. electrons at dose rates of 0.5 to 1.0 Mrad/min. The film was reequilibrated once with fresh permeating monomer vapor and subsequently reirradiated to give a larger graft content. The final overall graft content was 5.5% by weight, which is about 4.6% by volume of PVAc. The overall electron dose required was 5 Mrad. The amount of homopolymer formed that could be extracted by methanol or acetone was found to be less than 2% of the grafted polymer. Analysis of the modified membrane, to establish

the gradient shape, involves microtoming the membrane perpendicular to the thickness axis and determination by infrared techniques of the concentration of the grafted polymer in the individual slices. By employing this procedure it was found that the membrane used in this experiment possessed a nearly linear gradient of PVAc in PE.

Detailed discussions of the methods of measurement and calculations of the permeability, diffusion, and solubility coefficient have been published elsewhere.^{3,7,9,10} The experimental method used in this study was an adaptation of the high-vacuum gas transmission technique described by Barrer and Skirrow.¹¹ The film sample, mounted in a stainless-steel diffusion cell, was initially freed from dissolved atmospheric gases and any unreacted sorbed monomer and then exposed to a known pressure of the penetrant vapor at one surface, while essentially zero pressure was automatically maintained at the other surface. The increase of pressure with time in a constant-volume reservoir at the low-pressure side was measured with a sensitive diaphragm pressure transducer (Decker Corp. Model 306-2F) and recorded.

The penetrant used was methanol, spectroscopic grade. The solubility coefficient of methanol in PVAc was determined with a calibrated quartz-helix spring microbalance.

RESULTS AND DISCUSSION

The fluxes of penetrant along and against the grafted gradient of composition are shown in Figure 1. To elucidate these results, the generalized flux eqs. (1) will be examined and shown to account for this behavior.

Consider a polymer (component 2) membrane, $0 < x < 1$, in contact with a low molecular weight (component 1) penetrant reservoir at $x = 0$ and $x = 1$, respectively. The penetrant can dissolve in, and diffuse through, the polymer. If the flow of the penetrant, J_1 , is defined with respect to the center of mass movement, it can be shown⁶ that

$$J_1 = -L_{11}(d/dx)(\mu_2 - \mu_1) \quad (6)$$

when the chemical potential gradients of the individual components are the only forces considered, and coupling of nonconjugated flows and forces is neglected.

The modified membrane studied in this work possesses a gradient of composition along the diffusion axis; therefore, the chemical potential of the polymer (component 2) is an explicit function of the spatial coordinate x and *also* the vapor pressure p (equivalent to concentration in this experiment); hence,

$$\mu_2 = \mu_2(p, x) \quad (7)$$

$$d\mu_2/dx = (\partial\mu_2/\partial x) + (\partial\mu_2/\partial p)(dp/dx) \quad (8)$$

The chemical potential of the penetrant is dependent on vapor pressure (or concentration) only; thus, it is only implicitly position-dependent:

$$\mu_1 = \mu_1(p) \quad (9)$$

$$d\mu_1/dx = (\partial\mu_1/\partial p)(dp/dx) \quad (10)$$

Combining eqs. (6), (8), and (10) gives.

$$J_1 = -L_{11} [(\partial\mu_1/\partial p + \partial\mu_2/\partial p) dp/dx + \partial\mu_2/\partial x] \quad (11)$$

This equation predicts the directional preference effect, since $\partial\mu_2/\partial x$ is a "directional" quantity, adding to the flow in one direction while subtracting from it in the reverse direction. Whether the contribution of this factor is positive or negative will be determined by the relative directions of the gradient of grafted polymer in the membrane and the penetrant flow.

Since L_{11} , μ_1 , and μ_2 are not very accessible to experimental determination, an alternative approach can be used. This approach will exhibit the same functional behavior as eq. (11) but will describe the flow behavior of the system in readily measured experimental quantities.

Generally, grafting a polymer B which is soluble in a certain penetrant C onto a polymer membrane A which is essentially insoluble in C will result in a higher overall solubility of C in the modified membrane relative to pure A; i.e., the solubility properties of a membrane can be modified by grafting another polymer onto it. The overall solubility of the membrane will increase, if the grafted polymer is more soluble in the penetrant than the matrix polymer.

The diffusion characteristics of the membrane also will be affected by the grafted polymer. However, since diffusion is a kinetic quantity, the effect of the grafted polymer on the overall diffusion properties of the

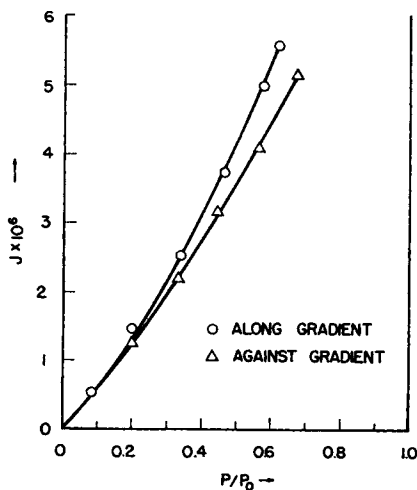


Fig. 1. Methanol fluxes [$\text{cm.}^3(\text{STP})/\text{cm.}^2/\text{sec.}$] along and against gradient of poly-(vinyl acetate) grafted onto the polyethylene membrane, versus relative vapor pressure (p/p_0).

membrane cannot be predicted as easily. The grafted polymer, presumably entirely in the amorphous phase, in which essentially all the solution and diffusion processes occur, can, at one extreme, act as a plasticizer, enhancing chain mobility and thus enhancing diffusion. At the other extreme, it can act as an inert filler, decreasing the overall volume available for diffusion and sorption and so decreasing the overall rate of transport.

In this experiment the grafted polymer, poly(vinyl acetate), is very soluble in the penetrant used, methanol, while the matrix polymer, polyethylene, is essentially insoluble in the penetrant. In the modified membrane the grafted polymer is solubilized by the penetrant but is not soluble in it, since it is chemically grafted to the matrix polymer. Further, the membrane used in this experiment possesses a gradient of composition. The poly(vinyl acetate) concentration varies continuously along the thickness coordinate, from a finite volume fraction of grafted polymer on one side to nil-grafted polymer on the other face.

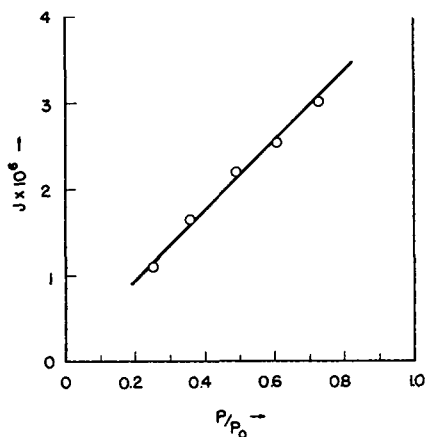


Fig. 2. Flux of methanol in polyethylene membrane versus relative vapor pressure (p/p_0).

Permeation is the result of two processes: diffusion, which is a mobility or kinetic process, and solubility, which is a thermodynamic quantity.^{3,10} Therefore, if the diffusion properties of the modified membrane are very similar to those of the pure matrix polymer, which will be true for low relative concentrations of grafted low molecular weight polymer, then the change in the solubility properties of the membrane will be the cause of change in permeation properties.

Examination of Figure 1 reveals that the permeation rates in the modified membrane, either along or against the gradient of composition, are higher than that in pure polyethylene (Fig. 2). This is to be expected, since the overall solubility of the penetrant in the modified membrane is always higher than that of the pure polyethylene membrane under the same experimental conditions.

The difference in rates along and against the gradient of composition is also expected, since in the case of permeation along the gradient of composition the high penetrant vapor-pressure side coincides with the high concentration of the soluble grafted-polymer side of the membrane. Since the solubility coefficient is a rising, continuous function of penetrant vapor pressure, the overall concentration of penetrant in the membrane in this case is higher than for permeation in the reverse direction: hence the faster rate when the composition and pressure gradients are of the same sign and direction.

The low radiation dose used in the preparation of the membrane is not expected to alter the crystalline morphology of the polyethylene.¹² The crosslinking resulting from the radiation is well below the level required to affect the transport properties of the penetrant used.¹⁰ The effect of the radiation on the transport properties of the membrane are thus discounted, and all outstanding effects are attributed to the presence of grafted polymer.

The diffusion coefficient of methanol in polyethylene is between one and two orders of magnitude higher than that in poly(vinyl acetate), i.e., 3.4×10^{-8} cm.²/sec. and about 1×10^{-9} cm.²/sec., respectively. The high radiation dose rate used in preparing the membrane, about 1.0 Mrad/min., is expected to yield a very low molecular weight grafted polymer.¹² This fact, coupled with the low overall concentration of poly(vinyl acetate) in the membrane, suggests that the diffusion mode and, hence, the diffusion coefficient are not greatly affected. The diffusion mode and coefficient in the modified membrane are thus very nearly the same as those in the pure matrix polymer. (Calculations based on $D = D_1\phi_1 + D_2\phi_2$, where $D_2\phi_2 \rightarrow 0$, corresponding to the case of inert filler, were carried out. The approach to the constraint that, at $x = 1$, $p = c = 0$, as will be discussed later, has been fulfilled to within less than 5% of initial vapor pressure.)

On the basis of these assumptions the modified membrane is one whose diffusion-kinetic properties essentially have not been altered, while its solution-thermodynamic properties have been greatly affected.

Fick's generalized law of diffusion is represented by

$$J = (d/dx) (Dc) \quad (12)$$

where J is the flux of the penetrant, D is a diffusion coefficient, and c is the concentration of the penetrant. The relation between the concentration of the penetrant and its vapor pressure is given by

$$c = Sp \quad (13)$$

where p is the vapor pressure of the penetrant, and S is a solubility coefficient.

Equations (12) and (13) are completely general, since no restrictions were imposed on the diffusion and solubility coefficients as to their concentration, temperature, and pressure dependence. For the membrane used in this experiment the diffusion coefficient is taken as that of methanol

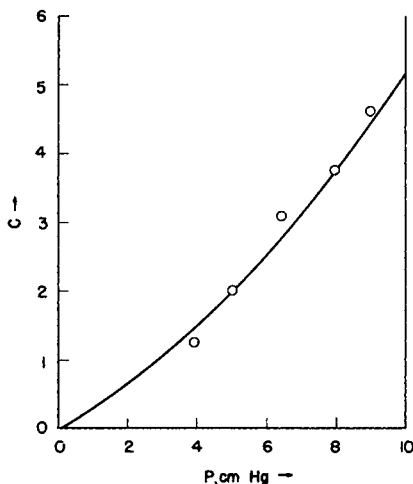


Fig. 3. Methanol uptake (g. of methanol per g. of polymer) by grafted polyethylene-poly(vinyl acetate) membrane [grafted poly(vinyl acetate) is 5% by volume] versus methanol vapor pressure (cm. Hg). The points are experimental results and the solid curve is $c = [\phi_1 S_1 + \phi_2 S_2]p$.

in pure polyethylene, which was found to be a constant (3.4×10^{-8} cm.²/sec. at 30°C.), independent of vapor pressure or concentration. The slight differences in diffusion coefficients due to slightly different morphological regions across the membrane are too small to affect the overall behavior and are neglected.

The solubility coefficient of the modified membrane must be some weighted function of the solubility coefficients of the pure components. In the concentration range of this experiment the sum of the volume fraction contributions of the two components.

$$S = \phi_1 S_1 + \phi_2 S_2 \quad (14)$$

where ϕ_i is the volume fraction of component i in the membrane, S_i the solubility coefficient of pure i , and S the solubility coefficient of the modified membrane, was shown (Fig. 3) to represent the solubility coefficient of the modified membrane very well.

The solubility coefficients of the pure components are a function of penetrant vapor pressure or concentration only. However, since the volume fractions at any point across the membrane thickness are explicit functions of the spatial coordinate, the solubility coefficient of the modified membrane is explicitly vapor-pressure-dependent (concentration-dependent) and position-dependent:

$$S = S(x, p) \quad (15)$$

Since we deal with time-independent rates (i.e., after the flux has reached steady-state), the vapor-pressure gradient in this case is only position-dependent:

$$p = p(x) \quad (16)$$

Combining (12) and (13), while $D = \text{constant}$, gives

$$J = -D[S (dp/dx) + p (dS/dx)] \quad (17)$$

but, from (15) and (16),

$$dS/dx = (\partial S/\partial x) + (\partial S/\partial p) (dp/dx) \quad (18)$$

Finally, combining (17) and (18) gives

$$J = -D \{ [S + p (\partial S/\partial p)] (dp/dx) + p (\partial S/\partial x) \} \quad (19)$$

The similarity between eqs. (19) and (11) can be verified upon inspection.

Equation (19), after rearrangement, is used to analyze the experimental results and elucidate the shape, direction, and sign of the different parameters involved. The rearranged differential equation, converted into a finite difference equation, to be used in an iteration computer program is:

$$\Delta p/\Delta x = [-(J/D) - p (\delta S/\delta x)]/[S + p (\delta S/\delta p)] \quad (20)$$

For the analysis of the experimental results all factors in the equation, with the exception of $\Delta p/\Delta x$, are known. Since the initial vapor pressure at the high-pressure face and the step size Δx , can be chosen as needed, the pressure gradient and, hence, concentration and solubility gradients can be found.

All the parameters on the right-hand side of eq. (20), except the flux J , are the results of, or can be calculated from, experiments involving the pure

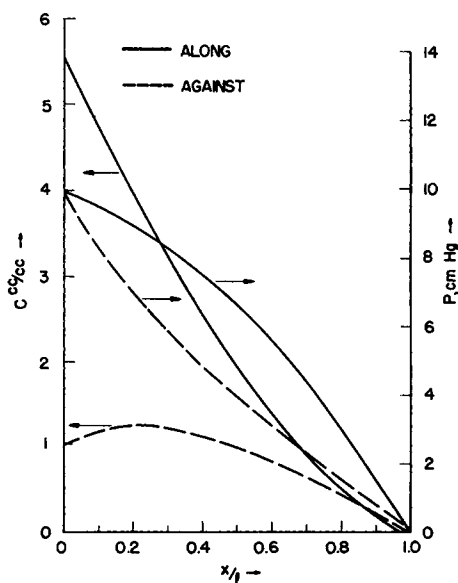


Fig. 4. Concentration (cm^3 of methanol vapor per cm^3 of polymer) and methanol vapor pressure (cm. Hg) along and against graft gradient, versus relative thickness.

components only. Thus, if this equation is proven to be a good representation of the behavior of the modified membrane, it subsequently can be used to predict the permeation behavior of any modified membrane, provided the solution properties of its components are known, and its composition at any point can be described explicitly.

TABLE I
Parameters for Transport of Methanol through Polyethylene-Graded Graft-Vinyl Acetate Film at 30°C.

$S_1 = 0.13 \exp\{-0.40(p/p_0)\}$	(Fig. 5)
$S_2 = 1.65 + 0.3(p)$	(Figs. 6, 7)
$\phi_2 = 1 - \phi_1$	
$= 0.1(x/1)$	(against gradient)
$= 0.1[1.0 - (x/1)]$	(along gradient)
$D = 3.4 \times 10^{-8}$ (cm. ² /sec.)	
J versus p_i	(Fig. 1)
$p_i =$ penetrant vapor pressure at high pressure side	

Since the low-pressure side is essentially at zero pressure at all times, the constraint on the calculation must be:

$$\text{At } x = 1, \quad p = c = 0 \quad (21)$$

This will be the end point of the analysis of the data calculation and the starting point for calculations carried out for the prediction of the behavior of modified membranes when the pure components' properties are known. In either case the relation

$$p_i = p_{i-1} + \Delta p \quad (22)$$

is used in conjunction with eq. (20). For the prediction calculation any flux J is chosen, and the required initial vapor pressure at $x = 0$ is found,

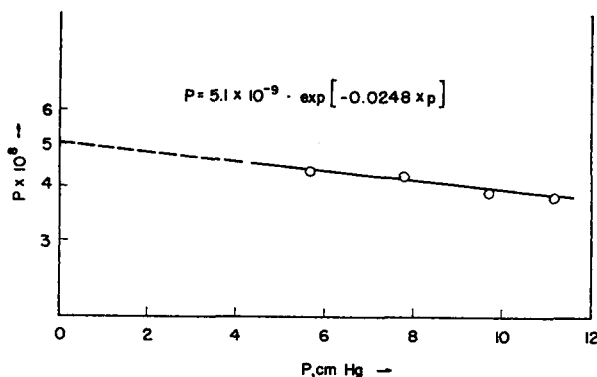


Fig. 5. Permeation constant [$\text{cm.}^3(\text{STP})/\text{cm.}^2/\text{cm.}/\text{sec.}/\text{cm. Hg}$] of methanol in polyethylene versus methanol vapor pressure (cm. Hg).

For the analysis the actual data are used (Table I) and constraint (21) must be fulfilled, if the model is correct. The agreement is evident in Figure 4.

Even if the diffusion coefficient were to be concentration- or activity-dependent, a slight modification of eq. (20), together with eq. (13) and the equation representing the concentration dependence or activity dependence of the diffusion coefficient, will yield the correct solution for this case.

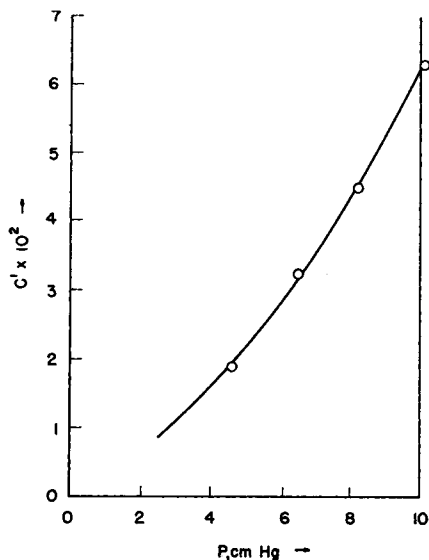


Fig. 6. Equilibrium sorption of methanol in poly(vinyl acetate). Methanol uptake [g. of methanol per g. of poly(vinyl acetate)] versus methanol vapor pressure (cm. Hg).

In the preceding treatment all coupling of nonconjugated flows and forces were neglected. It must be emphasized that this is allowed only because of the relative rates of flow of the different systems. It was found that the directional preference effect deteriorates with time, presumably owing to the onset on another gradient, possibly of stresses or structure, which counteracts the gradient of composition and eventually offsets it completely. However, the time required for the permeation experiments is far shorter than the time required for the deterioration of the directional preference phenomenon, and it is only in this relative time span that our assumptions and model are valid.

Conclusions

As was predicted,⁴⁻⁶ a membrane possessing solubility properties which are explicitly position-dependent exhibits the "value effect,"⁶ or directional preference to flow of penetrant. In a membrane with a grafted-composition gradient the diffusion and solution effects can be dealt with individually, if

the grafted polymer is of very low overall concentration and low molecular weight. Under these conditions the diffusion mode of the penetrant in the membrane is hardly affected by the grafted polymer, and the solubility coefficient of the modified membrane is the sum of the volume fraction

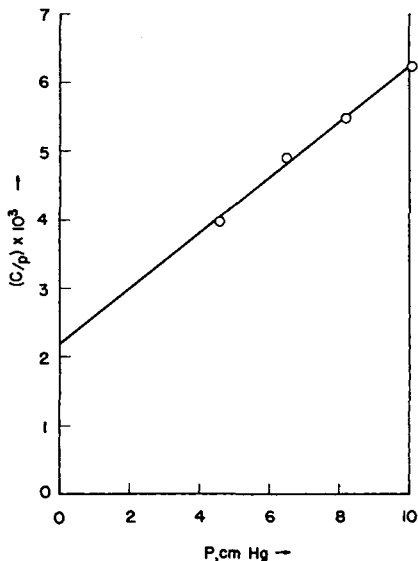


Fig. 7. Solubility of methanol in poly(vinyl acetate). Solubility coefficient [g. of methanol per g. of poly(vinyl acetate) per cm. Hg] versus methanol vapor pressure (cm. Hg).

contributions of the pure components. These facts allow one to use a simple mathematical description of the system to predict the behavior of any such membrane, provided the properties of the individual components comprising this membrane are known.

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