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MECHANISMS OF GAS PERMEATION THROUGH POLYMER MEMBRANES

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MECHANISMS OF GAS PERMEATION THROUGH POLYMER MEMBRANES

I. INTRODUCTION

The objective of the present study is to investigate the mechanisms by which gases are transported in and through polymer membranes, and the dependence of these mechanisms on pressure and temperature. This information is required for the development of new, energy-efficient membrane processes for the separation of industrial gas mixtures (1,2). Such processes are based on the selective permeation of the components of gas mixtures through nonporous polymer membranes.

Recent work has been focused on the permeation of gases through membranes made from glassy polymers, i.e., at temperatures below the glass transition of the polymers (T_g). Glassy polymers are very useful membrane materials for gas separations because of their high selectivity toward different gases.

To understand the overall mechanism of gas permeation, or transport, through polymer membranes it is necessary to investigate also the mechanisms of gas solution and diffusion in polymers (2-5), cf. Section II. During the past report period, a new theoretical model of gas solubility in glassy polymers was developed and tested with experimental data from the literature. This model describes satisfactorily the shape of solubility isotherms over wide ranges of pressure and temperatures, and is particularly useful for penetrant gases which plasticize (swell) glassy polymers. Of particular interest are recent observations that the solubility isotherms of such gases exhibit an inflection point at sufficiently high pressure, which indicates a change in the solution mechanism. Our model can quantitatively predict the penetrant pressure (or concentration) at which this inflection point occurs, and shows that it is due to a transition of the polymer from a glassy to a "rubbery" state at constant temperature.

The new model of gas solubility is based on concepts which are similar to those used successfully for many years to describe the viscoelastic behavior of polymers. These concepts are being extended to the transport of plasticizing gases in glassy polymers (by diffusion) and through polymer membranes by (permeation). The present study should have significant practical applications because the feed streams of many membrane separation processes contain gaseous components which strongly plasticize the polymer membranes, e.g., in the separation of CO_2 and H_2S from natural gas.

In addition, work has been continued to elucidate the unusual transport and solution behavior of light gases in poly(alkyl methacrylates). The gas permeability, diffusion, and solubility coefficients of these polymers do not appear to exhibit the strongly nonlinear dependence on pressure, or gas concentration, which is commonly observed with other polymers when the temperature is lowered through their T_g . This behavior was attributed to the very small "excess" free volume of the poly(alkyl methacrylates) in their glassy state. The free volume also affects the viscoelastic properties of the polymers.

II. GENERAL CONSIDERATIONS

A. Phenomenology of Gas Permeation

The permeation, or transport, of gases through nonporous polymer membranes generally occurs by a "solution-diffusion" mechanism (1-5), which is controlled by the molecular diffusion of the penetrant gas in the polymer matrix. Solution equilibrium is established between the penetrant in the gas phases in contact with the membrane interfaces and the penetrant dissolved in the membrane at these interfaces. The steady-state rate of permeation, J_s , through unit area of a homogeneous, isotropic, and planar (sheet) membrane of thickness, δ , when the pressures p_h and $p_l (< p_h)$ are maintained at the membrane interfaces, is given by the relation (1-4):

$$J_s = \bar{P}(p_h - p_l)/\delta, \quad (1)$$

where $\bar{P}$ is a mean permeability coefficient which depends on the nature of the penetrant/polymer system, the temperature and, in the most general case, on both p_h and p_l . It can be shown that (1-6):

$$P = \bar{D} \cdot S, \quad (2)$$

where $\bar{D}$ is a mean diffusion coefficient defined by the relation:

$$\bar{D} = \int_{c_l}^{c_h} D(c) dc / (c_h - c_l) \quad (3)$$

and (when $p_h > p_l$) S is a solubility coefficient defined by:

$$S = c/p ; \quad (4)$$

S is evaluated at pressure p_h . $D(c)$ is the local mutual diffusion coefficient for the penetrant/polymer system; c_h and c_l are the concentration of the penetrant dissolved at the membrane interfaces when pressures p_h and p_l , respectively, are maintained at these interfaces. $D(c)$ is a kinetic factor which depends on the size and shape of the penetrant molecules, the relative motions of the penetrant molecules and of the surrounding polymer chain segments, and the pertinent intermolecular forces. S is a thermodynamic factor which depends mainly on the intermolecular forces and, in the case of glassy polymers, on the "excess" free volume of the polymers.

Consequently, in order to elucidate the mechanisms of gas transport in and through polymers, it is necessary to determine $\bar{P}$, $\bar{D}$, and S for selected penetrant/polymer systems as a function of penetrant pressure (or concentration) and temperature. These measurements must be related to the chemical and physicochemical properties of the penetrant/polymer systems.

B. The Dual-Mode Sorption Model

The mechanisms of gas transport in polymers (by solution and diffusion) and across polymer membranes (by permeation) are known to be very different at temperatures above and below the glass transition temperature, T_g , of the polymers (1-5). The difference in these mechanisms is reflected in the significant differences observed in the dependence of $\bar{P}$, $\bar{D}$, and S on the pressure (or concentration) of the penetrant gases and on the temperature.

For example, the solubility of light gases (such as N_2 , CH_4 , and CO_2) in "rubbery" polymers, i.e., at temperatures above T_g , is often sufficiently low to be within the Henry's law limit. Therefore, the solubility coefficients, S , for such penetrant/polymers systems are independent of pressure, in some cases over a wide range of temperatures and pressures. $\bar{P}$ and

$\bar{D}$ for such systems also are independent of pressure (or concentration) or increase linearly with these variables. By contrast, $\bar{P}$, $\bar{D}$, and S for light gases in many "glassy" polymers, i.e., at temperatures below T_g , are highly nonlinear functions of the penetrant pressure (or concentration).

The nonlinear dependence of $\bar{P}$, $\bar{D}$, and S on penetrant pressure (or concentration) can be described satisfactorily in terms of a "dual-mode sorption" model (2-11). This model postulates that a gas dissolves in a glassy polymer consists of two distinct molecular populations:

- (1) Molecules dissolved in the polymer by an ordinary dissolution process similar to that above T_g , and
- (2) Molecules dissolved at a limited number of fixed sites, perhaps microcavities, in the polymer matrix.

The concentration of molecules dissolved by the ordinary dissolution process, c_D , is related to the penetrant equilibrium pressure, p , by a Henry's law isotherm:

$$c_D = k_D p, \quad (5)$$

where k_D is a solubility coefficient in the Henry's law limit. The concentration of molecules dissolved in microcavities, c_H , is related to p by the Langmuir isotherm:

$$c_H = c_H' b p / (1 + b p) \quad (6)$$

where c_H' is a "Langmuir saturation" constant, and b is a "Langmuir affinity" constant.

Local equilibrium is assumed to exist between the two molecular populations. The total concentration of the dissolved penetrant (the solubility), c , at a given p and temperature is then obtained from the sum of eqns. (9) and (10):

$$c = c_D + c_H = k_D p + c_H' b p / (1 + b p) \quad (7)$$

Equations (5), (6), and (7) are shown graphically for a hypothetical gas/polymer system in Figure 1. The overall solubility isotherm, i.e., the plot of c versus p represented by eqn. (7), is seen to be concave to the pressure axis. The solubility coefficient, S , is then obtained from

eqns. (4) and (7):

$$S(c) = c/p = k_D + c'_H b / (1 + bp); \quad (8)$$

S decreases with increasing p.

The solubility of most gases and vapors in polymer decreases with increasing temperature. This is due to the fact that the parameters k_D , c'_H , and b decrease in these cases as the temperature is raised; c'_H is zero above T_g , i.e., in the "rubbery" polymer state. Then, eqns (7) and (8) reduce, respectively, to the forms:

$$c = k_D p \quad (9) \quad \text{and} \quad S = k_H; \quad (10)$$

these relations are expressions of Henry's law.

C. Effects of Plasticizing Gases

Membrane processes are often used for the separation of gases with widely different critical temperatures. It is known that the higher the critical temperature of a gas, the higher is also its solubility in a polymer and its ability to plasticize (swell) the polymer. Plasticization generally modifies both the permeability and the selectivity of the polymer to different gases. A knowledge of these effects is important in the design of membrane separation processes.

Since permeation occurs by a solution-diffusion mechanism, it is necessary to determine the separate effects of plasticization on the penetrant solubility and diffusivity in a glassy polymer. The following discussion addresses the effects on the solubility.

It has been reported by Chiou, Maeda, and Paul (12,13) that the solubility isotherms for CO_2 in glassy poly(vinylidene fluoride)/poly(methyl methacrylate) blends exhibit an inflection point at higher penetrant gas pressures, cf. Figure 2. Similar results were reported more recently by Kamyia et al. (14) for the solubility of CO_2 in poly(vinyl benzoate) and poly(vinyl butyral), cf. Figure 3. The solubility isotherms of the above CO_2 /polymer systems at CO_2 pressures (or concentrations) below this inflection point are concave to the pressure axis and "history" dependent. Such a solubility behavior has been observed with CO_2 in a variety of other glassy polymers and can be described by the dual-mode sorption model (2-11). By contrast, at pressure

(or concentrations) above the inflection point the solubility isotherms are linear and reproducible, as has been observed with CO_2 in many "rubbery" polymers, i.e., at temperatures above their glass transition, T_g . Moreover, the linear segment of the solubility isotherms extrapolates to the origin of the solubility isotherms, i.e., of the c versus p plots.

Chiou and Paul (12,13) as well as Kamya et al. (14) have suggested that the inflection in the solubility isotherms is due to the plasticizing effect of CO_2 on the glassy polymers and polymer blends used in their studies. The effect of plasticization is to depress the glass-transition temperature, T_g , of a polymer. The above investigators further suggested that, at the penetrant pressure (or concentration) corresponding to the inflection point of a solubility isotherm, the T_g of the penetrant/polymer system is depressed to the experimental temperature of the isotherm. Therefore, the polymer is in the glassy state when the penetrant pressure (or concentration) is lower than that at the inflection point, and in the rubbery state at higher pressures (or concentrations). This hypothesis was confirmed by measurements of T_g as a function of the CO_2 concentration (14).

The above behavior can be attributed to the fact that the segmental motion of the polymer chains is enhanced and the chain-relaxation times are decreased with increasing penetrant concentration, and hence increasing plasticization, as was evidenced by ^{13}C NMR and stress-relaxation measurements. Therefore, the effect of an increase in the penetrant concentration in a polymer at constant temperature is similar to the effect of an increase in temperature.

The result of these effects is to depress the T_g of the polymer to an extent that will depend on the concentration of the penetrant in the polymer. Moreover, it is known that the solubility of most penetrant gases in glassy polymers decreases with increasing temperature. The above considerations suggest that the solubility of a plasticizing penetrant in a glassy polymer can also decrease at constant temperature when the penetrant concentration is increased, by a comparison with the solubility in an unplasticized polymer at the same p and T .

The present study has shown that the above effects of plasticization on the gas solubility in glassy polymers can be described by means of a new concept, which is described below.

III. THE TEMPERATURE-CONCENTRATION SUPERPOSITION PRINCIPLE (15)

The following discussion will consider first the solution of a gas in a glassy polymer

under hypothetical conditions where the penetrant does not significantly plasticize the polymer, i.e., it does not affect the segmental motions of the polymer chains and the spectrum of chain-relaxation times. The penetrant concentration, c , can then be expressed as a function of the penetrant pressure p by Henry's law:

$$c = S(0)p, \quad (11)$$

where $S(0)$ is a solubility coefficient in the Henry's law limit; $S(0)$ depends on the nature of the penetrant/polymer system and the temperature. Equation 1 is commonly valid at very low penetrant concentrations

If the penetrant gas plasticizes the glassy polymer, the penetrant concentration c (the solubility) will be lower than in the hypothetical case mentioned above, at the same pressure and temperature. The lower solubility may be attributed to the factors discussed in the previous section. Equation (11) must then be modified to the form:

$$c = S(c)p, \quad (12)$$

where $S(c)$ is a solubility coefficient which depends also on the penetrant concentration.

It is proposed to define a "shift factor" $\alpha_T(c)$ such that:

$$S(c) = S(0)\alpha_T(c) \quad (13)$$

Equations (12) and (13) then yield the relation

$$c = S(0)\alpha_T(c)p \quad (14)$$

The shift factor $\alpha_T(c)$ adjusts the gas solubility in the hypothetical unplasticized polymer, assumed to be represented by Henry's law [cf. eqn. (1)], to the actual solubility in the plasticized polymer at a given pressure and temperature. The temperature-concentration shift factor $\alpha_T(c)$ is similar in concept to the temperature shift factor $\alpha_T(T)$ used in polymer viscoelasticity. The latter adjusts the time scale of a particular relaxation function from a temperature T to a reference temperature T_0 (16).

The present study has shown that $\alpha_T(c)$ can be defined by a modified Doolittle equation (15), and therefore can be related to the free volume of the penetrant/polymer system (16). Equation (14) then takes the form:

$$c = S(0)p \exp \left\{ A \left[\frac{Tg(c)[Tg(c) - T(0)][Tg(0) - T]}{[Tg(0)]^2} \right] \right\}, \quad (15)$$

where A is a parameter which depends only on the nature of the penetrant/polymer system and the temperature; $Tg(0)$ is the glass-transition temperature of the pure polymer ($c=0$); $Tg(c)$ is the glass-transition temperature of the penetrant/polymer system when the penetrant concentration is c ; and T is the temperature of the solubility isotherm. $Tg(0)$ and $Tg(c)$ can be measured. $Tg(c)$ can also be estimated from the relation of Chou (17).

Equation (15) is a new expression for the solubility c of gases in glassy polymers at pressure p and temperature T . The agreement between eqn. (15) and published experimental data is very satisfactory, as can be seen from Figures 2 to 6. The entire solubility isotherm, including the inflection point, can also be predicted from eqn. (15), if the parameters A and $S(0)$ are known. Correlations for estimating the values of these parameters have been developed in this study (16).

IV. SUB-T_g CHANGES IN THE GAS SOLUBILITY MECHANISM IN POLY(ALKYL METHACRYLATES)

The permeability, diffusion, and solubility coefficients ($\bar{P}$, $\bar{D}$, and S , respectively) of light gases in "rubbery" polymers ($T > T_g$) are commonly independent of the penetrant gas pressure (or concentration in the polymers) if the polymers are not significantly plasticized. It was mentioned above that $\bar{P}$, $\bar{D}$, and S commonly become strongly nonlinear functions of pressure (or concentration) when the temperature is lowered below the T_g of the polymers. This behavior can be described by the dual-mode sorption model (2-10), and for S also by our new gas solubility model based on the "concentration-temperature superposition" principle. The onset of dual-mode sorption behavior is usually observed at temperatures closely below T_g .

It was reported previously that solubility measurements were performed in this laboratory

with Ar, CO₂, CH₄, and C₂H₆ in several poly(alkyl methacrylates) at elevated pressures, but no transition to dual-mode sorption behavior was observed at the T_g of these polymers. However, an onset of dual-mode sorption was observed at much lower temperatures, 30° to 65°C below T_g, depending on the polymer.

The above behavior was attributed to the fact that poly(alkyl methacrylates) have a much smaller "excess" free volume in the glassy state than other polymers, due to the higher mobility of their side chains. It was suggested that the values of the product $\Delta\alpha T_g$ offer a guide as to whether the onset of dual-mode sorption will occur just below T_g or at some lower temperature; $\Delta\alpha (= \alpha_r - \alpha_g)$, where α_r and α_g are the coefficients of thermal expansion of the polymer above and below T_g, respectively.

Recent solubility measurements with CO₂ in poly(ethyl methacrylate) indicate that the sub-T_g temperature at which the onset of dual-mode sorption behavior is observed is very sensitive to the previous "history" of the polymer. For example, the onset temperature may depend on whether or not the polymer was quenched to the experimental temperature from the rubbery state as well as on the rate of quenching, whether or not the polymer was "preconditioned" by exposure to the penetrant gas at elevated pressures, etc. The importance of these factors on the anomalous sub-T_g transitions to dual-mode sorption behavior is being investigated.

VI. PUBLICATIONS BASED ON THIS STUDY

In Print:

1. Stern, S.A., Vakil, U.M., and Mauze, G.R., "Solution and Transport of Light Gases in Poly(*n*-Butyl Methacrylate) in the Glass Transition Region. I. Absorption-Desorption Measurements", J. Polym. Sci.: Part B: Polym. Phys., 27(2), 405-429 (1989).
2. Zhou, S. and Stern, S.A., "The Effect of Plasticization on the Transport of Gases in and through Glassy Polymers", J. Polym. Sci.: Part B: Polym. Phys., 27, 205-222 (1989).
3. Subramanian, S. and Stern, S.A., "Dual-Mode Sorption Kinetics of Gases in Glassy Polymers", J. Polym. Sci.: Part B: Polym. Phys., 27, 1209-1220 (1989).
4. Stern, S.A., Zhou, S., Arauz-Lara, J.L., and Ware, B.R., "Evidence of Dual-Mode Diffusion of Small Molecules in Poly(1-Trimethylsilyl-1-Propyne) from Fluorescence Photobleaching Recovery", J. Polym. Sci.: Part C: Polym. Letters, 27, 427-431 (1989).
5. Zhou, S. and Stern, S.A., "Solubility of H₂ in Glassy Poly(vinyl acetate) at Elevated Pressure", J. Polym. Sci.: Part B: Polym. Phys., 50, 19-29 (1990).
6. Stern, S.A., and Trohalaki, S., "Fundamentals of Gas Diffusion in Rubbery and Glassy Polymers", Chap. 2 in "Barrier Polymers and Structures", W.J. Koros, Ed., ACS Symposium Series No. 423, American Chemical Society, Washington, D.C., 1990, pp.22-59.

Submitted for Publication

7. Zhou, S. and Stern, S.A., "Sub-Tg Changes in the Gas Solubility Mechanism in Poly(Alkyl Methacrylates)", Submitted for publication in J. Polym. Sci.: Part B: Polym. Phys.
8. Mi, Y., Zhou, S., and Stern, S.A., "Representation of Gas Solubility in Glassy Polymers by a Concentration-Temperature Superposition Principle", Submitted for publication in J. Polym. Sci.: Part B: Polym. Phys.

In Preparation

9. Itoh, K. and Stern, S.A., "Solution and Transport of Light Gases in Poly (*n*-Butyl Methacrylate) in the Glass Transition Region. II. Time-Lag Measurements".
10. Stern, S.A. and R. Vaidyanathan, "Solution and Transport of Light Gases in Poly (Ethyl Methacrylate). Absorption-Desorption Measurements".

REFERENCES

1. S.A. Stern, Chapt. 1 in "Synthetic Membranes", M.B. Chenoweth, Ed., MMI Press Symposium Series, Vol. 5, Harwood Academic Publishers, NY, 1986, pp. 1-37.
2. V.J. Koros and R.T. Chern, Chapt. 20 in "Handbook of Separation Process Technology", R.W. Rousseau, Ed., Wiley-Interscience, New York, 1987, pp. 862-953.
3. S.A. Stern and H.L. Frisch, Ann. Revs. Mater. Sci., 11, 523 (1981).
4. H.L. Frisch and S.A. Stern, Crit. Revs. Solid State and Mater. Sci., 11(2), 173(1983), CRC Press, Boca Raton, FL.
5. S.A. Stern and S. Trohalaki, Chapt. 2 in "Barrier Polymers and Structures", ACS Symposium Series No. 423, American Chemical Society, Washington, D.C. 1990, pp. 22-59.
6. W.R. Vieth, J.M. Howell, and J.H. Hsieh, J. Membrane Sci., 1, 177 (1976).
7. D.R. Paul and W.J. Koros, J. Polym. Sci., Polym. Phys. Ed., 14, 675 (1976).
8. W.J. Koros and D.R. Paul, J. Polym. Sci., Polym. Phys. Ed., 16, 1947 (1978).
9. D.R. Paul, Ber. Bunsenges, Phys. Chem., 83, 294 (1979).
10. W.J. Koros, D.R. Paul, and G.S. Huvard, Polym., 20, 956 (1974).
11. W.R. Vieth, Chapt. 2 and 3 in "Membrane Systems: Analysis and Design", Hanser Publishers, New York, 1989, pp. 9-66.
12. J.S. Chiou, Y. Maeda, and D.R. Paul, J. Appl. Polym. Sci., 30, 4019 (1984).
13. J.S. Chiou and D.R. Paul, J. Appl. Polym. Sci., 32, 2897 (1986).
14. Y. Kamiya, K. Mizoguchi, Y. Naito, and T. Hirose, J. Polym. Sci.: Part B: Polym. Phys., 24, 535 (1986).
15. Y. Mi, S. Zhou, and S.A. Stern, Submitted for publication in Macromolecules.
16. J.D. Ferry, "Viscoelastic Properties of Polymers", 34d Ed., J. Wiley and Sons, New York, 1980.
17. T.S. Chow, Macromolecules 13, 362 (1980).
18. T.A. Barbari, W.J. Koros, and D.R. Paul, J. Polym. Sci.: Part B: Polym. Phys., 26, 729 (1988).

Figure 1. "Dual-mode" sorption (solubility) isotherm for gases in glassy polymers.
All isotherms are for the same temperature.

Figure 2. Solubility isotherms for CO₂ in 35% and 50% PVF₂/PMMA blends at 35°C [13]. PVF₂=Poly(vinylidene fluoride); PMMA=Poly(methyl methacrylate).

The solid curves drawn through the data points were calculated from eqn. (15).

Figure 3. Solubility isotherms for CO₂ in poly(vinyl benzoate) (PVB) at 25, 35, and 45°C. Open and filled symbols represent absorption and desorption, respectively [14].

The solid curves drawn through the data points were calculated from eqn. (15).

Figure 4. Solubility isotherms for CO₂ in poly(ethylene terephthalate) (PET) at several temperatures [18].

The solid curves drawn through the data points were calculated from eqn. (15).
The isotherm at 85°C exhibits an inflection point.

Figure 5. Solubility isotherms for N_2 in various polymers at $35^\circ C$ [18].
 PEI=Polyetherimide; PC=Polycarbonate; PA=Polyarylate; PH=polyhydroxyether.

The solid curves drawn through the data points were calculated from eqn. (15).

Figure 6. Solubility isotherms for CH₄ in various polymers at 35°C [18].

PEI=Polyetherimide; PC=Polycarbonate; PA=Polyarylate; PH=polyhydroxyether.

The solid curves drawn through the data points were calculated from eqn. (15).

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