

NOTE

Isotherm Shape for Penetrant Sorption in Glassy Polymers

INTRODUCTION

It is well known that amorphous polymer-penetrant systems exhibit different sorption isotherms above and below the glass transition temperature of the pure polymer, T_{g2} . For penetrant sorption in rubbery polymers, the sorption isotherms curve away from the pressure axis as the penetrant pressure is increased so that¹

$$\left(\frac{\partial^2 p_1}{\partial \omega_1^2}\right)_T < 0 \quad (1)$$

where p_1 is the pressure of the penetrant (component 1) in the gas phase and ω_1 is the mass fraction of the penetrant in the liquid phase. For penetrant sorption in glassy polymers, the sorption isotherms generally curve toward the pressure axis with increasing gas pressure so that²

$$\left(\frac{\partial^2 p_1}{\partial \omega_1^2}\right)_T > 0 \quad (2)$$

However, Smith and Schmitz³ have noted that the isotherm for the sorption of water into glassy poly(methyl methacrylate) (PMMA) appears to have a shape described by eq. (1) rather than by eq. (2). The shape of their sorption isotherm is consistent with sorption data reported previously by Bueche⁴ and by Barrie and Machin.⁵ On the other hand, significant negative departures from volume additivity have been reported⁶ for the water-glassy PMMA system, and these density data are typical of volumetric behavior for glassy polymer-penetrant systems.

Recently, a model has been proposed⁶⁻⁹ for understanding the volumetric and sorption behavior of a system composed of a glassy polymer and a penetrant. This model is based on the premise that the molecular structure of the system is modified as a penetrant is added to a glassy polymer. The equations of this model have been recently used to provide a reasonably good description of the volumetric behavior for the water-glassy PMMA system.⁶ The purpose of this note is to illustrate that the proposed approximate model predicts that the shape of the sorption isotherm for a glassy polymer-penetrant system depends on whether the penetrant is a good or poor solvent for the particular polymer of interest. In addition, it is shown

that the proposed model provides a reasonably good description of sorption isotherms for the water-glassy PMMA system.

THEORY

The proposed model⁶⁻⁹ permits us to study quantitatively how changes in polymer structure affect the volumetric and sorption behavior of a glassy polymer-penetrant system. This model is based on a simple sample preparation history with the expectation that reasonable predictions for the properties of glassy polymer-penetrant systems can be obtained in cases when these properties are not overly sensitive to the exact nature of the sample preparation history. If the gas phase is ideal, the sorption process in the glassy polymer⁹ is described by the following equations:

$$\frac{p_1}{p_1^0} = \phi_1 \exp(\phi_2 + \chi \phi_2^2) e^F \quad (3)$$

$$F = \frac{M_1 \omega_2^2 (\hat{C}_p - \hat{C}_{pg}) A}{RT} \left(\frac{T}{T_{gm}} - 1 \right) \quad (4)$$

Here, ω_2 is the mass fraction of the polymer (component 2), T is the temperature of the sorption process, \hat{C}_p is the specific heat capacity at constant pressure for the equilibrium liquid polymer, \hat{C}_{pg} is the specific heat capacity at constant pressure for the glassy polymer, and p_1^0 is the vapor pressure of the pure liquid penetrant at T . Also, M_1 is the molecular weight of the penetrant, and χ is the interaction parameter of the Flory-Huggins theory.¹⁰ The parameter χ can be a function of temperature but not of concentration. The volume fractions of penetrant and polymer, ϕ_1 and ϕ_2 , are defined using the expressions

$$\phi_1 = \frac{\omega_1}{\omega_1 + q\omega_2} \quad (5)$$

$$\phi_2 = \frac{q\omega_2}{\omega_1 + q\omega_2} \quad (6)$$

$$q = \frac{\hat{V}_2^0}{\hat{V}_1^0} \quad (7)$$

where \hat{V}_1^0 is the specific volume of the pure penetrant in the liquid state and \hat{V}_2^0 is the specific volume of the pure

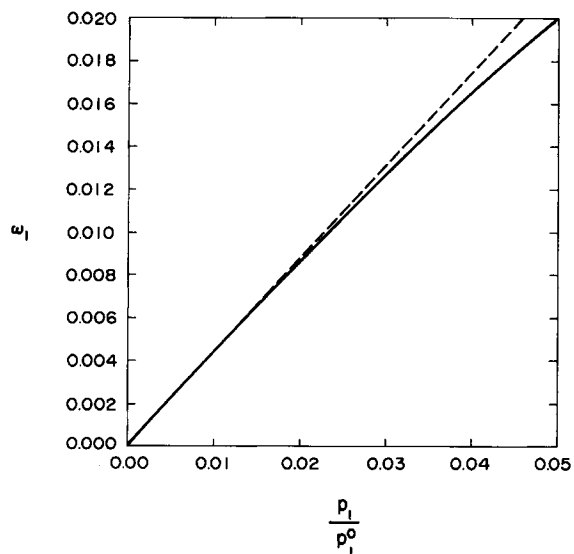


Figure 1 Sorption isotherm for water-PMMA system at $T = 296$ K with $\chi = 0.25$. The solid line is the prediction of the theory, and the dashed line is a straight line tangent to this prediction at $\omega_1 = 0$.

equilibrium liquid polymer. Finally, it is assumed that T_{gm} , the glass transition temperature of the polymer-penetrant mixture at a particular penetrant mass fraction, can be calculated using the following linear approximation:

$$T_{gm} = T_{g2} - A\omega_1 \quad (8)$$

where the coefficient A is dependent on the nature of the penetrant which is used to depress the glass transition temperature of a particular polymer.

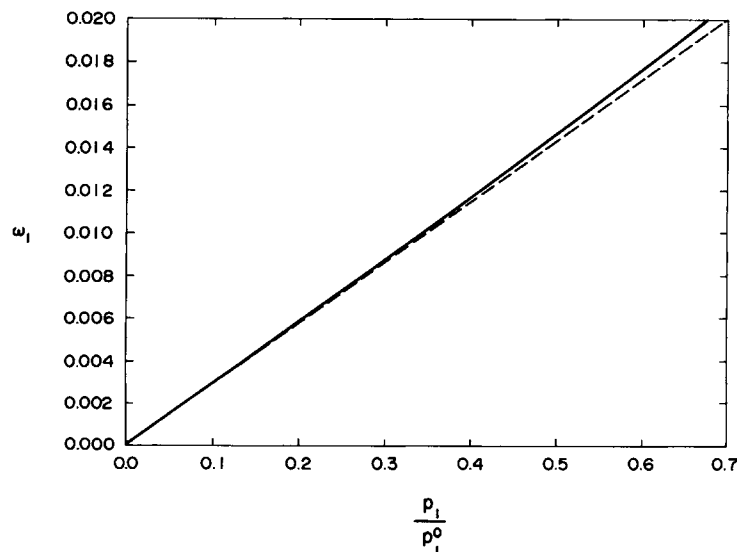


Figure 2 Sorption isotherm for water-PMMA system with $T = 296$ K and $\chi = 3$. The meaning of the solid and dashed lines is given in the caption to Figure 1.

If, for convenience, we set $q = 1$, it can easily be shown for a glassy polymer-penetrant system that

$$\frac{1}{p_1^0} \left(\frac{\partial^2 p_1}{\partial \omega_1^2} \right)_{\omega_1=0} = 2e^{1+\chi} e^{F_0} \left\{ -(1 + 2\chi) + \frac{M_1}{RT} \times (\hat{C}_p - \hat{C}_{pg}) A \left[\frac{AT}{T_g^2} + 2 \left(1 - \frac{T}{T_{g2}} \right) \right] \right\} \quad (9)$$

where F_0 is the value of F evaluated at $\omega_1 = 0$. The first term in the brackets on the right-hand side of eq. (9) is negative, and the second term is positive. Hence, the sign of the second pressure derivative at $\omega_1 = 0$ depends on the magnitude of the interaction parameter χ . For low values of χ (a good solvent for the polymer), the second derivative at $\omega_1 = 0$ is generally positive, and the isotherm shape is of a form that is characteristic of sorption in glassy polymer-penetrant systems [eq. (2)]. For high values of χ (a poor solvent for the polymer), the second derivative at $\omega_1 = 0$ is generally negative, and the isotherm shape resembles a sorption isotherm for penetrant sorption in a rubbery polymer [eq. (1)], even though the sorption process involves a glassy polymer.

RESULTS AND DISCUSSION

Sorption isotherms at appropriate temperatures T can be computed for the water-glassy PMMA system using the following values³ of the parameters for this system: $M_1 = 18$ g/mol, $\hat{C}_p - \hat{C}_{pg} = 0.0760$ cal/g°C, $q = 0.818$, $T_{g2} = 393.5$ K, $A = 1100$ K, and an appropriate value of χ . Sorption isotherms for the water-glassy PMMA system at 296 K are presented in Figures 1 and 2. In Figure 1, a value of $\chi = 0.25$ is utilized, and it is evident that the

shape of the isotherm is described by eq. (2). Hence, the sorption process at this low value of χ leads to a sorption isotherm shape that is typically observed for glassy polymer-penetrant systems. On the other hand, when a relatively large value of χ is utilized ($\chi = 3$), it is evident from Figure 2 that the shape of the isotherm is described by eq. (1). Hence, in this case, the isotherm is of a form typically observed in rubbery polymer-penetrant systems even though a glassy polymer is being utilized.

An estimate of the value of χ for the water-PMMA system can be obtained from the sorption data of Brauer and Sweeney¹¹ near the glass transition temperature of the pure polymer. From these data on water sorption in liquid PMMA, a value of $\chi = 3.45$ was obtained, and it is of interest to use this value to see how well the proposed theory describes water sorption in glassy PMMA. Comparisons of theoretical predictions with experimental data from three investigations³⁻⁵ are presented in Figures 3-5. All of the predictions are made at the appropriate temperatures using the above properties for the water-PMMA system with one exception. In Figure 5, a value of $T_{g2} = 365$ K was utilized since this is the value reported in the paper of Barrie and Machin.⁵ Figures 3-5 illustrate that the proposed theory yields reasonably good predictions for the sorption isotherms for the water-glassy PMMA system, especially when consideration is taken of the fact that the theory has no adjustable parameters. Furthermore, it appears that the high value of χ for the water-PMMA system makes the isotherm for water sorption in glassy PMMA resemble the form usually observed for penetrant sorption in rubbery polymers.

Differences between theoretical predictions and the experimental data may be caused by clustering effects in

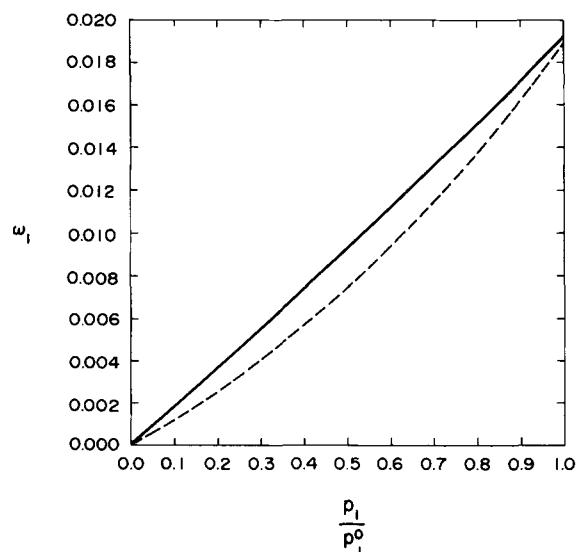


Figure 3 Comparison of the theoretical prediction (solid line) for the sorption isotherm for the water-PMMA system at $T = 296$ K with the experimental data of Smith and Schmitz³ (dashed line).

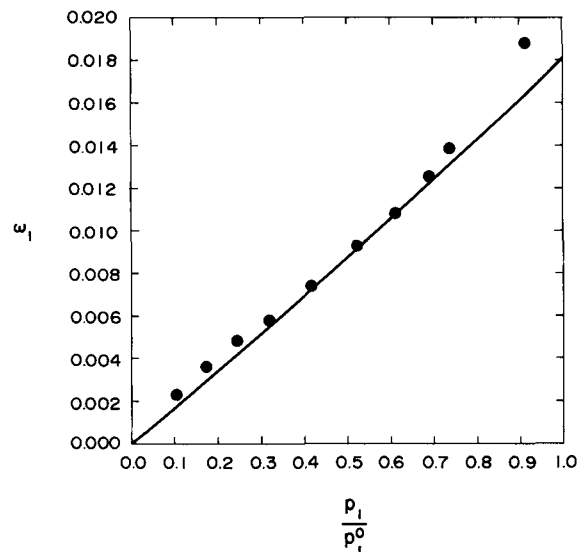


Figure 4 Comparison of the theoretical prediction (solid line) for the sorption isotherm for the water-PMMA system at $T = 303$ K with the experimental data of Bueche⁴ (solid points).

the water-PMMA system. The Flory-Huggins theory, which is used to form the glassy isotherm, does account for the clustering of water molecules but perhaps not ac-

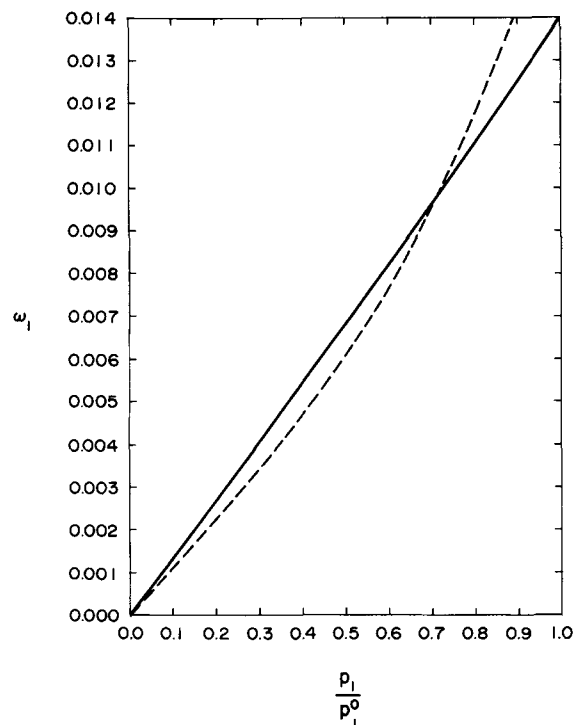


Figure 5 Comparison of the theoretical prediction (solid line) for the sorption isotherm for the water-PMMA system at $T = 313.7$ K with the experimental data of Barrie and Machin⁵ (dashed line).

curately enough.¹ However, it is also well known¹² that clustering for the water-PMMA system is important only for relative pressures higher than 0.75. The principal objective of this paper is to illustrate that the new sorption theory can predict rubbery type sorption isotherms for sorption in glassy polymers. Application of the theory to the water-PMMA system shows that such predictions are possible even if exact quantitative agreement with the data is not achieved.

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References

1. J. S. Vrentas, J. L. Duda, and S. T. Hsieh, *Ind. Eng. Chem. Prod. Res. Dev.*, **22**, 326 (1983).
2. D. Raucher and M. D. Sefcik, *Am. Chem. Soc. Symp. Ser.*, **223**, 111 (1983).
3. L. S. A. Smith and V. Schmitz, *Polymer*, **29**, 1871 (1988).
4. F. Bueche, *J. Polym. Sci.*, **14**, 414 (1954).
5. J. A. Barrie and D. Machin, *Trans. Faraday Soc.*, **67**, 244 (1971).
6. J. S. Vrentas and C. M. Vrentas, *J. Polym. Sci. Polym. Phys. Ed.*, **28**, 241 (1990).
7. J. S. Vrentas, J. L. Duda, and H.-C. Ling, *Macromolecules*, **21**, 1470 (1988).
8. J. S. Vrentas and C. M. Vrentas, *Macromolecules*, **22**, 2264 (1989).
9. J. S. Vrentas and C. M. Vrentas, *Macromolecules*, **24**, 2404 (1991).
10. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953.
11. G. M. Brauer and W. T. Sweeney, *Mod. Plast.*, **32**, 138 (1955).
12. H. W. Starkweather, *J. Polym. Sci. Polym. Lett.*, **1**, 133 (1963).

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