Evaluation of a Sorption Equation for Polymer–Solvent Systems

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SYNOPSIS

The predictive capabilities of a proposed sorption equation for describing the sorption behavior of glassy polymer–penetrant systems is evaluated. Factors determining the shapes of isotherms for glassy polymer–penetrant systems are considered. Data–theory comparisons are presented for three glassy polymer–penetrant systems. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

An important aspect of the study of mass-transfer processes in polymer–solvent systems is the nature of the sorption isotherm for the polymer–penetrant mixture. Data on penetrant sorption in rubbery polymers indicate that the sorption isotherms curve away from the pressure axis as the penetrant pressure is increased so that[1]

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

Here, p_1 is the pressure of the penetrant (component 1) in the gas phase; ω_1, the mass fraction of the penetrant in the liquid phase; and T, the temperature of the sorption process. On the other hand, for penetrant sorption in glassy polymers, two different types of behavior have been observed: For some polymer–penetrant systems (see Fig. 1), the sorption isotherms for penetrant sorption in glassy polymers[2] curve toward the pressure axis with increasing gas pressure so that

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

For other cases[3] of penetrant sorption in glassy polymers (see Figs. 2 and 3), the sorption isotherms

are described by eq. (1). Consequently, any realistic sorption equation for polymer–penetrant systems must predict behavior described by eq. (1) for penetrant sorption in rubbery polymers and must be flexible enough to predict that penetrant sorption in glassy polymers can be described by either eq. (1) or (2), depending on the nature of the polymer–penetrant system under consideration.

Recently, an equation was proposed for describing sorption behavior in polymer–penetrant systems.[4] This equation is based on a model that has been formulated for describing the volumetric and sorption behavior of a system composed of a glassy polymer and a penetrant.[4-8] It is assumed in this model that the molecular structure of the system is modified as a penetrant is added to a glassy polymer, and the model thus produces predictions on how changes in polymer structure affect the volumetric and sorption behavior of the system. Since the model is based on a particular preparation history for the polymer–solvent sample, reasonable predictions should be obtained for the sorption and volumetric behavior when the sorption and volumetric properties are not overly sensitive to the exact nature of the sample preparation history.

Previously, it was shown[4] that the new sorption equation gave good predictions for the sorption behavior of the glassy polycarbonate–carbon dioxide mixture, a system with the sorption isotherm described by eq. (2). Furthermore, it was recently shown[8] that reasonably good predictions were obtained for the sorption behavior of the glassy poly(methyl methacrylate)–water mixture, a system described by eq. (1). The purpose of this article was

to evaluate further the predictive capabilities of the proposed sorption equation in describing the sorption behavior of the three glassy polymer–penetrant systems presented in Figures 1–3. In particular, the ability of the new equation to predict the correct shape of the sorption isotherm for a particular glassy polymer–solvent system will be examined and the ability of this equation to provide a good quantitative description of the sorption isotherm will be evaluated. In addition, factors determining the shapes of isotherms for glassy polymer–penetrant systems will be considered. The sorption equation is briefly described in the second section of the paper, and data–theory comparisons are presented in the third section.

THEORY

For the sake of simplicity, we present the sorption equation for cases where the following assumptions are valid:

1. The concentration dependence of T_{gm} (the glass transition temperature of the polymer–penetrant mixture at a particular penetrant mass fraction) can be represented by the following linear approximation:

$$T_{gm} = T_{g2} - A\omega_1 \qquad (3)$$

Here, T_{g2} is the glass transition temperature of the pure polymer, and A, a constant that depends on the nature of the penetrant that is used to depress the glass transition temperature of a particular polymer.

2. The pressure in the gas phase is low enough so that the gas phase is ideal.

3. Pressure effects on the penetrant chemical potential in the liquid phase are negligible.

When these assumptions are valid, the sorption process is described by the following set of equations:

$$\frac{p_1}{p_1^0} = \phi_1 \exp(\phi_2 + \chi\phi_2^2)e^F \qquad (4)$$

$$F = \frac{M_1\omega_2^2(\hat{C}_p - \hat{C}_{pg})A}{RT}\left(\frac{T}{T_{gm}} - 1\right) \quad T < T_{gm} \qquad (5)$$

$$F = 0 \quad T \geq T_{gm} \qquad (6)$$

Here, p_1^0 is the vapor pressure of the liquid penetrant at T; $\hat{C}_p$, the specific heat capacity at constant pres-
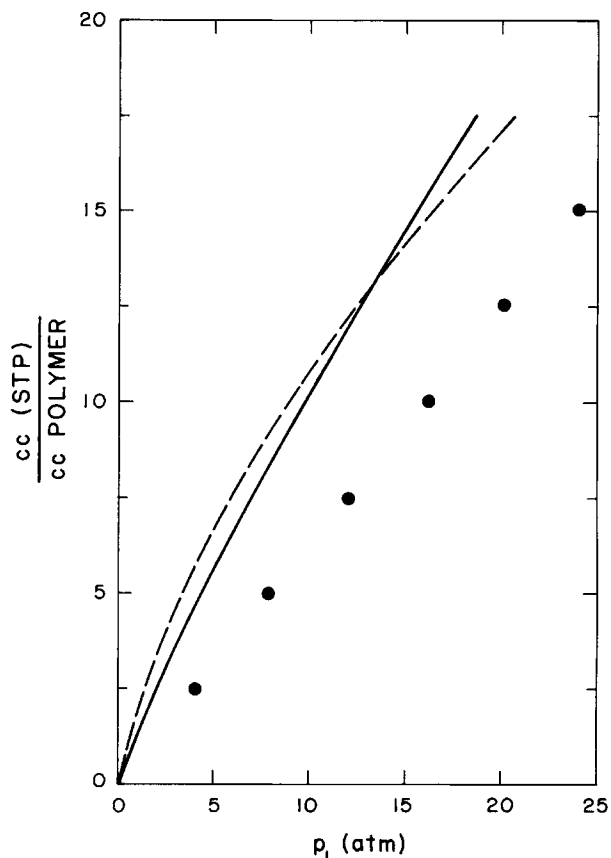

Figure 1 Theoretical and experimental[2] sorption isotherms for the polystyrene–carbon dioxide system at 35°C. The solid line is the prediction of the proposed sorption theory, the dashed line is a representation of the experimental data, and the solid circles are the predictions of the Flory–Huggins theory.

sure for the equilibrium liquid polymer; $\hat{C}_{pg}$, the specific heat capacity at constant pressure for the glassy polymer; M_1, the molecular weight of the penetrant; and ω_2, the mass fraction of the polymer (component 2). Also, χ is the interaction parameter of the Flory–Huggins theory.[9] It may be a function of temperature but not of concentration. Finally, the following expressions define ϕ_1 and ϕ_2, the volume fractions of penetrant and polymer, respectively:

$$\phi_1 = \frac{\omega_1}{\omega_1 + q\omega_2} \qquad (7)$$

$$\phi_2 = \frac{q\omega_2}{\omega_1 + q\omega_2} \qquad (8)$$

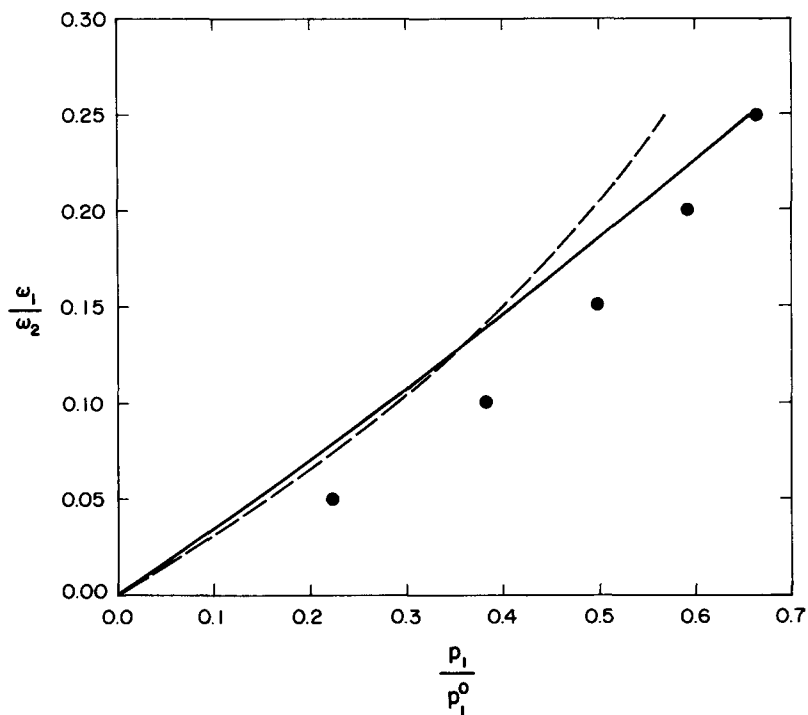$$q = \frac{\hat{V}_2^0}{\hat{V}_1^0} \qquad (9)$$

Figure 2 Theoretical and experimental[3] sorption isotherms for polystyrene–benzene system at 25°C. See Figure 1 legend for symbols.

Here, $\hat{V}_1^0$ is the specific volume of the pure penetrant in the liquid state; and $\hat{V}_2^0$, the specific volume of the pure equilibrium liquid polymer. More general equations can be used when the above three as-sumptions are relaxed. These are presented else-where.[4]

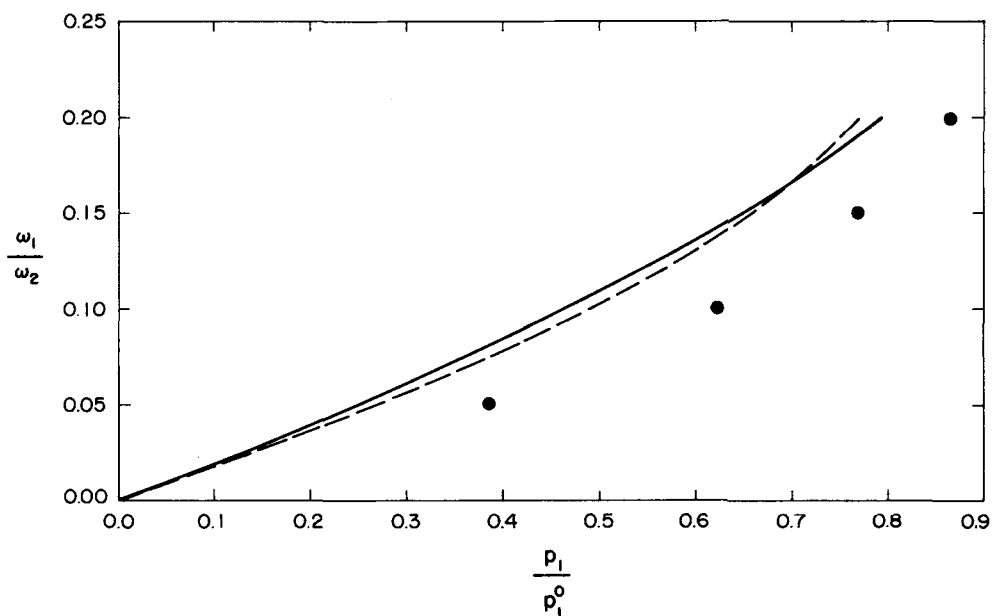From the above set of equations, it is evident that predictions of sorption behavior can be made using

Figure 3 Theoretical and experimental[3] sorption isotherms for polystyrene–methyl ethyl ketone system at 25°C. See Figure 1 legend for symbols.

four polymer properties (T_{g2}, $\hat{C}_p$, $\hat{C}_{pg}$, $\hat{V}_2^0$), three penetrant properties (M_1, p_1^0, $\hat{V}_1^0$), and two properties of the polymer–penetrant system (A and χ). The polymer and penetrant properties are generally available with the possible exception of $\hat{V}_1^0$ and p_1^0 for gaseous penetrants significantly above their critical temperatures. Data are available for A for some polymer–penetrant systems,[10] and the theoretical expression derived by Chow[11] for the dependence of T_{gm} on ω_1 can also be utilized. The parameter χ is often available,[12] and it also can be estimated from solubility parameter considerations.[12,13] In addition, sorption predictions for a glassy polymer–penetrant system can be made using a χ value obtained from data for sorption of the penetrant of interest in the rubbery polymer. Clearly, the sorption theory is a predictive theory since there are no adjustable parameters.

DATA–THEORY COMPARISONS

Data–theory comparisons are carried out here for the sorption of three penetrants, carbon dioxide, benzene, and methyl ethyl ketone, in polystyrene. Vapor pressures for the three penetrants and density data for benzene and methyl ethyl ketone can be obtained from a standard data source.[14] A value of $\hat{V}_1^0 = 0.85$ cm^3/g was used for carbon dioxide since this appears to be a reasonable estimate for carbon dioxide sorption in another polymer: polycarbonate.[4,5] Density data for liquid polystyrene were obtained from information provided by Höcker et al.[15] Also, values of $T_{g2} = 373$ K and $\hat{C}_p - \hat{C}_{pg} = 0.062$ cal/g °C were used[10,11,16] for polystyrene. A value of $A = 370$ K was used for the polystyrene–benzene system. This value was estimated from data presented by Ferry.[10] A value of $A = 370$ K was also used for the polystyrene–methyl ethyl ketone system, but this parameter was obtained in a less direct manner by using glass transition data for the polystyrene–ethyl acetate system[10] and critical concentration estimates for ethyl acetate and methyl ethyl ketone in polystyrene.[3] A value of $A = 690$ K for the polystyrene–carbon dioxide system was determined from data presented by Chiou et al.[17] A value of $\chi = 0.46$ was used for the polystyrene–benzene system,[12] and a value of $\chi = 1$ was used for the polystyrene–methyl ethyl ketone system.[18] For the polystyrene–carbon dioxide system, data for carbon dioxide sorption in molten polystyrene[19,20] were used to obtain an estimated value of $\chi = 2$. This value had a possible error of 30% because there were significant differences in the solubility data reported

in the two investigations[19,20] for carbon dioxide sorption in molten polystyrene. All the property values used in determining the predictions of the theory were thought to be reasonably good estimates, the most questionable values being the χ and $\hat{V}_1^0$ values for carbon dioxide, the A value for methyl ethyl ketone, and the χ value for benzene.

The calculations of the sorption isotherms for the liquid penetrants (benzene and methyl ethyl ketone) were carried out using eqs. (3)–(5) since the penetrant pressures were low. For carbon dioxide sorption, it was necessary to replace eq. (4) with a high-pressure version presented elsewhere[4] since relatively high pressures were used for this gaseous penetrant. Comparisons of theory and experiment are presented in Figures 1–3. These figures contain experimental data, the predictions of the new sorption theory, and the predictions of the Flory–Huggins theory [eq. (4) with $F = 0$]. The experimental sorption isotherms for benzene and methyl ethyl ketone are described by eq. (1), and the experimental sorption isotherm for carbon dioxide is described by eq. (2). It is evident from Figures 1–3 that the new sorption theory produces the correct isotherm shape in all three cases. In addition, for all three penetrants, there are significant differences between the sorption data and the predictions of the Flory–Huggins theory. This is, of course, to be expected since there is no reason to expect that this theory will describe sorption in glassy polymers. On the other hand, the new theory provides reasonably good predictions for the sorption behavior of these three penetrants; the worst errors were observed for the benzene–polystyrene system at the highest pressures. The value of $\chi = 0.46$ used for the polystyrene–benzene system was based on data[12] near $\phi_2 = 0$, whereas the sorption isotherm is measured at high polymer concentrations. A different value of χ may be more appropriate in the vicinity of $\phi_2 = 1$.

The above sorption data indicate that different types of sorption behavior are observed for glassy polymer–penetrant systems. In some cases, the sorption isotherms are described by eq. (1), and, in other cases, eq. (2) gives the correct description of the sorption process. It is of interest to determine what factors influence the shape of the sorption isotherm in glassy polymers. Clearly, as noted previously,[8] the interaction parameter χ plays an important role, but perhaps the most important factor is the value of the parameter A. Sorption isotherms for two typical polymer–solvent systems are presented in Figure 4. The properties of the two systems are identical with the exception of parameter A. The top curve in Figure 4 represents a polymer–solvent

system with $A = 1000$ and $X = 1$, and the bottom curve represents a system with $A = 100$ and $X = 1$. Clearly, the sorption isotherm for $A = 1000$ is described by eq. (2), and the sorption isotherm for $A = 100$ is described by eq. (1). It is evident that the isotherm shape changes significantly as A increases, shifting from a curve described by eq. (1) to one described by eq. (2). It is reasonable to expect that gaseous penetrants have higher values of A for a particular polymer since they should contribute more free volume to the mixture and, hence, cause a greater reduction in the glass transition temperature of the system. Consequently, penetrants that are gases at room temperature should have relative high values of A and isotherms described by eq. (2). Penetrants that are liquids at room temperature will generally have lower values of A and isotherms described by eq. (1). It appears that previous sorption studies in glassy polymers have been concerned mostly with gaseous penetrants and isotherms described by eq. (2) (see Fig. 1). Sorption studies with liquid penetrants with isotherms described by eq. (1) (see Figs. 2 and 3) have largely been ignored when theories have been proposed for the sorption process. It is fair to conclude that the proposed sorption theory cannot only provide the correct shape of a sorption isotherm for penetrant sorption in a glassy polymer but also a reasonably good quantitative description of the isotherm.
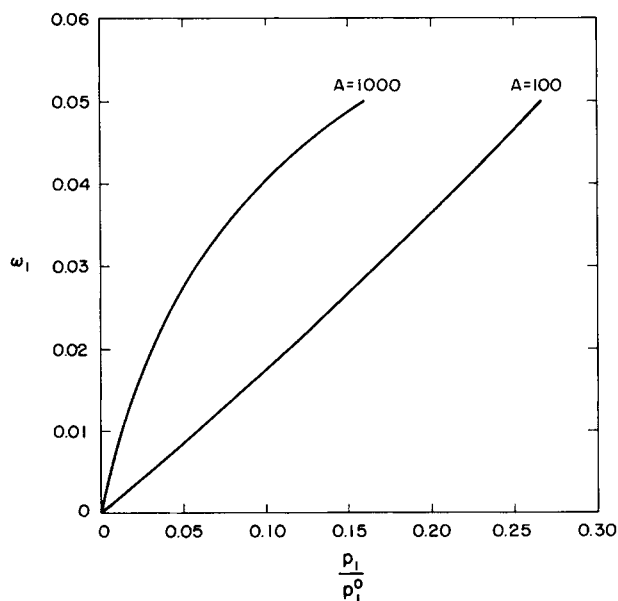
Finally, it is important to note that all experimental data reported in Figures 1–3 are for glassy polymer–solvent mixtures since the temperature of the experiment is, in all cases, less than the glass transition temperature of the polymer–penetrant mixture. Hence, the curvature observed in Figures 2 and 3 cannot be attributed to the existence of a rubbery polymer–solvent system.

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Figure 4 Dependence of sorption isotherms on A for typical polymer-solvent system with $X = 1$.