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Hysteresis Effects for Sorption in Glassy Polymers

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ABSTRACT: A theory based on taking into account structural rearrangements of the polymer matrix is used to analyze hysteresis effects that have been observed during a penetrant absorption−desorption cycle in a glassy polymer. A previously developed theoretical description for the absorption process is used as a basis for developing equations describing volumetric and isotherm data for the desorption process. A different sample history is used for desorption experiments, and this difference in sample history leads to different volumetric and sorption behavior. The theoretical predictions are compared with volumetric and isotherm data for the glassy polycarbonate−carbon dioxide system.

Introduction

Amorphous polymer−penetrant systems generally exhibit significantly different sorption and volumetric behavior above and below the glass transition temperature of the pure polymer, T_{g2}. In a series of recent papers,[1−7] a theory has been proposed for describing the volumetric and sorption behavior of penetrant *absorption* in a glassy polymer. The objective of this paper is to propose a theoretical description of volumetric and sorption behavior during penetrant *desorption* in a glassy polymer and hence to describe hysteresis effects that have been observed during a penetrant absorption−desorption cycle.[8] The theory for the absorption process is reviewed in the second section of this paper, and the theory for the desorption process is developed in the third section. The predictions of the theory are compared with experimental data in the fourth section of this paper.

Absorption Behavior

The model for describing volumetric and sorption behavior for the absorption process for glassy polymer−penetrant systems is based on the following assumptions:[1−7]

(1) The thermodynamic behavior for the pure polymer is characterized by the following four thermodynamic variables: α_2, the thermal expansion coefficient for the equilibrium liquid polymer; α_{2g}, the thermal expansion coefficient for the glassy polymer; $\hat{C}_p$, the specific heat capacity at constant pressure for the equilibrium liquid polymer; and $\hat{C}_{pg}$, the specific heat capacity at constant pressure for the glassy polymer. All of these thermodynamic variables are assumed to be independent of polymer molecular weight, and they can be approximated by average values in the temperature ranges under consideration. In general, different temperature ranges can of course lead to somewhat different average values. It is further assumed that structural differences in the polymer glass will not affect α_{2g} and $\hat{C}_{pg}$ significantly. Finally, rapid changes in the thermal expansion coefficient and in the specific heat near T_{g2} are idealized as step changes from α_{2g} to α_2 and from $\hat{C}_{pg}$ to $\hat{C}_p$ at T_{g2}.

(2) The polymer−penetrant mixture, at a given penetrant concentration, exists as a nonequilibrium liquid structure at temperatures below T_{gm}, the glass transition temperature of the polymer−penetrant mixture at a particular penetrant mass fraction. It is assumed that, once this structure is formed at a given penetrant concentration and temperature, the structure remains effectively invariant during any experiments carried out on the polymer−penetrant mixture until the concentration level is changed. Structural relaxation at a given penetrant concentration and temperature is assumed to be negligible over the time scale of the usual sorption experiment.

(3) For an equilibrium liquid mixture of polymer and penetrant, the specific volume of the mixture, $\hat{V}$, is given by the expression

$$\hat{V} = \omega_1 \hat{V}_1^0 + \omega_2 \hat{V}_2^0 \tag{1}$$

at a given concentration for temperatures both above and below T_{gm}. The following expression can be used for the specific volume of a glassy polymer−penetrant mixture below T_{gm}:

$$\hat{V} = \omega_1 \hat{V}_1^0 + \omega_2 \hat{V}_{2g}^0 \tag{2}$$

In these equations, $\hat{V}_1^0$ is the specific volume of the pure penetrant in the liquid state, $\hat{V}_2^0$ is the specific volume of the pure equilibrium liquid polymer, $\hat{V}_{2g}^0$ is the appropriate specific volume of the glassy polymer used to form the nonequilibrium liquid mixture at a given temperature below T_{gm}, and ω_I is the mass fraction of component I. In this paper, the subscript 1 refers to the penetrant and the subscript 2 to the polymer. The above equations are based on the assumption of volume additivity, but the quantity $\hat{V}_{2g}^0$ is a function of penetrant concentration. Indeed, it is the concentration dependence of $\hat{V}_{2g}^0$ which dictates the nature of the volumetric behavior of the polymer−penetrant mixture below T_{gm}. For example, if an ideal specific volume for a glassy polymer−penetrant mixture is defined as follows

$$\hat{V}(\text{ideal}) = \omega_1 \hat{V}_1^0 + \omega_2 \hat{V}_{2g}^0(\omega_1{=}0) \tag{3}$$

then an excess specific volume, $\Delta\hat{V}$, for the glassy polymer−penetrant system at a particular mass fraction can be determined by using the following expression:

$$\Delta\hat{V} = \hat{V}(\text{actual}) - \hat{V}(\text{ideal}) \tag{4}$$

Clearly, the concentration dependence of $\hat{V}_{2g}^0$ can lead

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to an apparent departure from volume additivity. In addition, an apparent partial specific volume of the penetrant, $\hat{V}_1$, can be computed at $\omega_1 = 0$ using the equation[2]

$$\hat{V}_1(\omega_1{=}0) = \left(\frac{\partial \hat{V}}{\partial \omega_1}\right)_{\omega_1=0} + \hat{V}^0_{2g}(\omega_1{=}0) \tag{5}$$

It is clear that the concentration dependence of $\hat{V}^0_{2g}$ leads to a partial specific volume of the solvent which is different than the specific volume of the pure solvent.

(4) For the liquid polymer–penetrant mixture, the specific Gibbs free energy, $\hat{G}$, can be expressed as

$$\hat{G} = \omega_1 \hat{G}^0_1 + \omega_2 \hat{G}^0_2 + \Delta \hat{G}_m \tag{6}$$

whereas $\hat{G}$ for a glassy polymer–penetrant mixture is given by the following expression:

$$\hat{G} = \omega_1 \hat{G}^0_1 + \omega_2 \hat{G}^0_{2g} + \Delta \hat{G}_m \tag{7}$$

In these equations, $\hat{G}^0_1$ is the specific Gibbs free energy of the penetrant in the liquid state, $\hat{G}^0_2$ is the specific Gibbs free energy of the equilibrium liquid polymer, $\hat{G}^0_{2g}$ is the appropriate specific Gibbs free energy of the glassy polymer used to form the nonequilibrium liquid mixture below T_{gm}, and $\Delta\hat{G}_m$ is the Gibbs free energy of mixing per mass of mixture at some temperature T. For the present purpose, it is convenient to use the Flory–Huggins result[9] for $\Delta\hat{G}_m$:

$$\Delta \hat{G}_m = RT\left[\frac{\omega_1}{M_1}\ln \phi_1 + \frac{\omega_2}{M_2}\ln \phi_2 + \frac{\chi \omega_1 \phi_2}{M_1}\right] \tag{8}$$

$$\phi_1 = \frac{\omega_1}{\omega_1 + q\omega_2} \tag{9}$$

$$\phi_2 = \frac{q\omega_2}{\omega_1 + q\omega_2} \tag{10}$$

$$q = \hat{V}^0_2/\hat{V}^0_1 \tag{11}$$

Here, R is the gas constant, ϕ_I is the volume fraction of component I, M_I is the molecular weight of component I, and χ is the interaction parameter of the Flory–Huggins theory. Consequently, it can be shown[5] that $\hat{G}_1$, the partial specific Gibbs free energy of the penetrant in the polymer–penetrant mixture, is given by the expression

$$\hat{G}_1 = \hat{G}^0_1(T,p_1) + \frac{RT}{M_1}[\ln \phi_1 + \phi_2 + \chi \phi_2^2] \tag{12}$$

for $T \geq T_{gm}$ and by the equation

$$\hat{G}_1 = \hat{G}^0_1(T,p_1) + \omega_2^2\left(\frac{\partial \hat{G}^0_{2g}}{\partial \omega_1}\right)_{T,p_1} + \frac{RT}{M_1}[\ln \phi_1 + \phi_2 + \chi \phi_2^2] \tag{13}$$

for $T < T_{gm}$. Here, p_1 is the pressure of the penetrant in the essentially pure gas phase above the mixture. Again, it is the concentration dependence of $\hat{G}^0_{2g}$ which dictates the nature of the sorption process below T_{gm}.

(5) It is convenient to assume that the concentration dependence of T_{gm} can be represented by a linear approximation if the penetrant concentration is not too high:

$$T_{gm} = T_{22} - A\omega_1 \tag{14}$$

In this equation, the coefficient A depends on the characteristics of the penetrant which is used to depress the glass transition temperature of a particular polymer.

(6) It is assumed that the only effect of polymer molecular weight on the sorption process is its influence on T_{g2}. The dependence of T_{g2} on polymer molecular weight M_2 can be expressed as follows

$$T_{g2}(M_2) = T_{g2}(\infty) - \frac{B}{M_2} \tag{15}$$

where B is an appropriate constant for a particular polymer.

(7) The values of $\hat{V}^0_{2g}$ and $\hat{G}^0_{2g}$ and their variations with concentration depend on how the polymer–penetrant system is prepared since the structure and hence the properties of glassy polymers are dependent on the sample history. For an absorption experiment, it is supposed that the polymer–penetrant mixture is formed by first mixing the materials at some temperature above T_{gm} and then using a conventional experimental time scale to cool the system to the desired temperature below T_{gm}. Furthermore, it is assumed that the thermal properties α_{2g} and $\hat{C}_{pg}$ of the polymer in the polymer–penetrant mixture are the same as those for the pure polymer as it is cooled below T_{g2}. For this sample history, it is then possible to derive the following equation for the concentration dependence of $\hat{V}^0_{2g}$:[2]

$$\hat{V}^0_{2g} = \hat{V}^0_2(T_{g2})[1 - A\alpha_2\omega_1 + \alpha_{2g}(T - T_{g2} + A\omega_1)] \tag{16}$$

Also, eqs 4 and 5 yield the following results:

$$\Delta \hat{V} = -A\omega_1\omega_2\hat{V}^0_2(T_{g2})(\alpha_2 - \alpha_{2g}) \tag{17}$$

$$\hat{V}_1(\omega_1{=}0) = \hat{V}^0_1 - A\hat{V}^0_2(T_{g2})(\alpha_2 - \alpha_{2g}) \tag{18}$$

In addition, the ratio of V_m, the total volume of a glassy polymer–penetrant mixture, to V_0, the volume of the pure polymer, can be computed using eq 16 and the following equation:

$$\frac{V_m}{V_0} = \frac{\dfrac{\omega_1}{1-\omega_1}\hat{V}^0_1 + \hat{V}^0_{2g}(\omega_1)}{\hat{V}^0_{2g}(\omega_1{=}0)} \tag{19}$$

For the absorption process, it can be shown[5] that the sorption isotherm can be expressed as follows:

$$\frac{p_1}{p^0_1} = \phi_1 \exp[\phi_2 + \chi\phi_2^2]e^F \tag{20}$$

$$F = \frac{M_1\omega_2^2(\hat{C}_p - \hat{C}_{pg})A}{RT}\left(\frac{T}{T_{gm}} - 1\right) \qquad T < T_{gm} \tag{21}$$

$$F = 0 \qquad T \geq T_{gm} \tag{22}$$

Here, p^0_1 is the vapor pressure of the pure liquid penetrant at T. These equations are valid at pressures which are low enough so that the gas phase is ideal and so that pressure effects on the penetrant chemical potential in the liquid phase can be neglected. Equations which include these effects are presented elsewhere.[5] Finally, the following equation can be derived[5] for the molar heat of solution, $\Delta\tilde{H}$, for the penetrant in the glassy polymer:

$$\Delta\tilde{H} = -\frac{RT^2}{p_1^0}\frac{\partial p_1^0}{\partial T} - RT^2\frac{\partial \chi}{\partial T} - M_1(\hat{C}_p - \hat{C}_{pg})A \quad (23)$$

All of the above assumptions are of course utilized in the derivation of equations describing volumetric and sorption behavior for a penetrant absorption process, and the first six will also be used to analyze volumetric and sorption behavior for a penetrant desorption process. The sample preparation history used for the absorption process is not adequate for the desorption process, and, hence, the seventh assumption must be modified appropriately. Before this is done (in the next section), it is useful to compare the predictions of the equations derived for the absorption process with experimental data in order to establish the general viability of the proposed method. A data−theory comparison for penetrant absorption can be summarized as follows:

(1) Equation 17 of the proposed theory predicts significant negative departures from volume additivity, and this has been observed experimentally. Indeed, the predicted values of $\Delta\hat{V}$ are in reasonably good agreement with experimental $\Delta\hat{V}$ values for four glassy polymer−diluent systems[10,11] and for the glassy poly(methyl methacrylate)−water system.[4]

(2) Equation 18 predicts that the apparent partial specific volume of the penetrant can be significantly less than the specific volume of the pure penetrant. This prediction has been observed experimentally.[8,10,11]

(3) The theoretical predictions[3] of eq 19 for the polycarbonate−carbon dioxide system are in reasonably good agreement with volumetric absorption data for this system.[8]

(4) The theory based on eq 20 for the sorption process predicts that sorption isotherms become more nearly linear as the temperature increases,[5] and this prediction is consistent with experimental data.[10−14]

(5) The theory based on eqs 15 and 20 predicts that the penetrant sorption at a given pressure increases as the polymer molecular weight increases and that the sorption isotherms become more nearly linear as the polymer weight decreases.[5] These predictions are consistent with experimental observations.[14]

(6) The theory predicts that the sorption isotherms can change shape with increasing penetrant concentration, and this change occurs at lower penetrant concentrations as the temperature increases. These predictions are consistent with experimental observations.[15]

(7) From eq 23 of the theory, it is evident that the penetrant dissolution process in a glassy polymer is more exothermic than the dissolution process for the same gas in the rubbery form of the polymer.[5] This prediction is consistent with heat of solution data reported by Meares.[16]

(8) The theory predicts that the sorption isotherm given by eq 20 can have different shapes. For penetrant sorption in rubbery polymers (eqs 20 and 22), the theory predicts that the sorption isotherms curve away from the pressure axis as the penetrant pressure is increased so that

$$\left(\frac{\partial^2 p_1}{\partial \omega_1^2}\right)_T < 0 \quad (24)$$

This result is consistent with experimental isotherms for rubbery polymers.[8,17] For penetrant sorption in glassy polymers (eqs 20 and 21), the theory predicts that the sorption isotherms can curve toward the pressure axis with increasing gas pressure so that

$$\left(\frac{\partial^2 p_1}{\partial \omega_1^2}\right)_T > 0 \quad (25)$$

However, the theory also predicts that isotherms described by eq 24 are also possible for penetrant sorption in glassy polymers, depending on the values of A and χ. For low values of χ, the theory predicts that isotherms described by eq 25 are likely for glassy polymers, but, for large values of χ, isotherms described by 24 are possible. For the glassy poly(methyl methacrylate)−water system, the theory predicts that the isotherms should take the shape given by eq 24 since $\chi = 3.45$ for this system. In this case, the isotherm is in a form typically observed in rubbery polymer−penetrant systems even though the polymer is in a glassy state. The predicted isotherms are in reasonably good agreement with the experimental sorption data.[6] In addition, for high values of A (generally for gaseous penetrants), the isotherm shape is described by eq 25, whereas for low values of A (generally for liquid penetrants), the isotherm shape is described by eq 24. Hence, the theory predicts isotherms described by eq 25 for the glassy polycarbonate−carbon dioxide and glassy polystyrene−carbon dioxide systems and isotherms described by eq 24 for sorption of benzene and methyl ethyl ketone in glassy polystyrene. The predicted shapes are in agreement with the experimental shapes, and the predicted isotherms are in reasonably good agreement with the experimental isotherm data.[5,7]

The above summary provides ample evidence of the general validity of the theory, and it remains to attempt to include the effect of sample history on the theoretical predictions. It is important to note that the theory for the absorption process is predictive because there are no adjustable constants and no need to use volumetric or sorption data for the glassy polymer−penetrant mixture to evaluate any of the physical properties.

Desorption Behavior

In a typical absorption experiment for a glassy polymer, the dry polymer is taken to the temperature of interest (after being cooled from the liquid to the glassy state), and the penetrant is added by utilizing a step increase in pressure. A wide pressure range can be covered by using a series of step-change experiments. The sample preparation history used in the theoretical development in the second section for absorption experiments is of course somewhat different, although it also involves the sequential addition of penetrant. Since the predictions of the absorption form of the theory are in reasonable agreement with experimental volumetric and sorption data, it appears that the volumetric and sorption behavior of the system is not overly sensitive to the exact sample preparation history when penetrant is added to the system. However, a desorption process of course involves the removal of the penetrant, and it is likely that this difference in sample history will lead to different volumetric and sorption behavior. Indeed, Fleming and Koros[8] reported very significant hysteresis effects in volumetric and sorption data for an absorption−desorption cycle. In addition, the dry polymer had more unrelaxed volume (and hence a different structure) after completion of the cycle. Consequently, a different model of the polymer structure must be used for the desorption experiment.

It is postulated here that the desorption process begins at temperature T with an equilibrium polymer−penetrant mixture at the penetrant mass fraction, $(\omega_1)_E$, at which $T = T_{gm}$:

$$(\omega_1)_E = \frac{T_{g2} - T}{A} \tag{26}$$

Since the polymer−penetrant mixture is at its effective glass transition temperature, any removal of penetrant will immediately form a glassy mixture. It is assumed that the polymer−penetrant system exists in a random close packing configuration[18,19] at $(\omega_1)_E$ with a fractional occupied volume of 0.64. It is further assumed that, because of the glassy nature of the mixture, only the occupied volume collapses as penetrant is removed from the system. Hence, it is easy to show that the specific volume of the glassy polymer after complete removal of the penetrant is given by the following expression:

$$[\hat{V}^0_{2g}(\omega_1{=}0)]_D = \hat{V}^0_2(T) + \frac{0.36\hat{V}^0_1(T)(\omega_1)_E}{1 - (\omega_1)_E} \tag{27}$$

From eq 16, it is evident that the specific volume of the glassy polymer before an absorption experiment is simply

$$[\hat{V}^0_{2g}(\omega_1{=}0)]_A = \hat{V}^0_2(T_{g2})[1 + \alpha_{2g}(T - T_{g2})] \tag{28}$$

where the subscripts A and D refer to absorption and desorption experiments, respectively. In general, eqs 27 and 28 produce different specific volumes and hence different structures for the glassy polymer, and this difference will lead to different volumetric and sorption behavior.

Since the above postulate leads to an estimate of structural differences in the glassy polymer for the absorption and desorption experiments, we can now introduce a model for the desorption process by introducing the following two assumptions:

(1) It is assumed that the deviations of the polymer glass from the equilibrium liquid state for a desorption experiment are proportional to the deviations for an absorption experiment:

$$[\hat{V}^0_{2g}(\omega_1,T)]_D - \hat{V}^0_2(T) = k_1\{[\hat{V}^0_{2g}(\omega_1,T)]_A - \hat{V}^0_2(T)\} \tag{29}$$

$$[\hat{G}^0_{2g}(\omega_1,T)]_D - \hat{G}^0_2(T) = k_2\{[\hat{G}^0_{2g}(\omega_1,T)]_A - \hat{G}^0_2(T)\} \tag{30}$$

Consequently, it can be shown that the desorption counterpart to eq 16 is simply

$$[\hat{V}^0_{2g}]_D = \hat{V}^0_2(T_{g2})[1 + \alpha_2(T - T_{g2}) + k_1(\alpha_{2g} - \alpha_2)(T - T_{g2} + A\omega_1)] \tag{31}$$

Furthermore, the proportionality constant k_1 can be calculated using eq 27 and the following expression:

$$k_1 = \frac{[\hat{V}^0_{2g}(0,T)]_D - \hat{V}^0_2(T_{g2})[1 + \alpha_2(T - T_{g2})]}{\hat{V}^0_2(T_{g2})(\alpha_{2g} - \alpha_2)(T - T_{g2})} \tag{32}$$

In addition, it is evident from eq 30 that

$$\left[\left(\frac{\partial \hat{G}^0_{2g}}{\partial \omega_1}\right)_{T,p_1}\right]_D = k_2\left[\left(\frac{\partial \hat{G}^0_{2g}}{\partial \omega_1}\right)_{T,p_1}\right]_A \tag{33}$$

so that the isotherm for the desorption process is given by the following expression:

$$\left[\frac{p_1}{p_1^0}\right]_D = \phi_1 \exp[\phi_2 + \chi\phi_2^2] \exp[k_2 F] \tag{34}$$

Only the proportionality constant k_2 is unknown at this stage of the development.

(2) It is assumed that the quantities $[\hat{V}^0_{2g}(0,T) - \hat{V}^0_2(T)]$ and $[\hat{G}^0_{2g}(0,T) - \hat{G}^0_2(T)]$ serve to characterize the glassy polymeric structure at all temperatures so that a glassy structure formed by a desorption process at temperature T is equivalent to a glassy structure formed by cooling the polymer for an absorption experiment to some temperatures T_D. Hence, it can be shown that the temperature T_D which produces a structure for an absorption sample which is equivalent to the desorption structure at T is given by the expression

$$T_D = T_{g2} + \frac{k_1(T - T_{g2})(\alpha_{2g} - \alpha_2)_A}{(\alpha_{2g} - \alpha_2)_D} \tag{35}$$

In this equation, different average values of α_2 are used for the temperature ranges T_{g2} to T and T_{g2} to T_D. Hence, from eq 30 and from previous results[5] for the temperature dependence of $\hat{G}^0_{2g}(0,T)$, the following equation can be derived for the proportionality constant k_2:

$$k_2 = \frac{\left[(T_D - T_{g2}) - T_D \ln\left(\frac{T_D}{T_{g2}}\right)\right]}{\left[(T - T_{g2}) - T \ln\left(\frac{T}{T_{g2}}\right)\right]} \tag{36}$$

As is the case for the theory for absorption behavior, there are no adjustable constants for the theory describing the desorption process.

Volumetric behavior for the absorption process can be predicted using eqs 16 and 19, and volumetric behavior for a desorption experiment can be predicted using eqs 19, 26, 27, 31, and 32. In each case, the dependence of V_m/V_0 on ω_1 can be computed at a given temperature T if values of $\hat{V}^0_1(T)$, $\hat{V}^0_2(T)$, $\hat{V}^0_2(T_{g2})$, α_2, α_{2g}, T_{g2}, and A are available. All of these parameters with the possible exception of A are generally available. If no data on the dependence of T_{gm} on ω_1 exist for a given polymer−penetrant system, then it is possible to use[5] an approximate theoretical expression derived by Chow[20] for the dependence of T_{gm} on ω_1.

Sorption isotherms for the absorption process can be computed using eqs 9−11, 14, 20, and 21, and the prediction of sorption isotherms for a desorption experiment involves utilization of eqs 9−11, 14, 21, and 34−36 and the value of k_1 calculated from the volumetric equations. The dependence of p_1/p_1^0 on ω_1 can be determined for a given temperature T for each case if values of χ, $\hat{C}_p$, $\hat{C}_{pg}$, and the parameters listed above are

Table 1. Properties of the Polycarbonate−Carbon Dioxide System at 35 °C

property	value	property	value
T_{g2}	150.4 °C	$\hat{V}_1^0$	0.85 cm^3/g
A	1110 K	$\hat{V}_2^0$	0.8135 cm^3/g
α_2	5.16×10^{-4} K^{-1}	$\hat{V}_2^0(T_{g2})$	0.865 cm^3/g
α_{2g}	2.59×10^{-4} K^{-1}	$\hat{C}_p - \hat{C}_{pg}$	0.055 cal/(g °C)
		χ	1.64

available. Usually, only the value of χ may not be available, and this quantity can be estimated using solubility parameter considerations.[5]

Results and Discussion

The predictions of the absorption and desorption theories are now compared with the volumetric and sorption data reported by Fleming and Koros[8] for an absorption−desorption cycle for the glassy polycarbonate−carbon dioxide system at 35 °C. Data−theory comparisons were carried out previously for the volumetric absorption data[3] over the complete experimental concentration range and for the absorption isotherm[5] for mass fractions up to $\omega_1 = 0.05$. The concentration range for the sorption isotherm was limited because the linear prediction for T_{gm} (eq 14) was significantly different than the T_{gm} versus ω_1 dependence calculated using the theory of Chow[20] for $\omega_1 > 0.05$. Differences in the T_{gm} versus ω_1 relationship generally have a small effect on volumetric predictions, but sorption predictions are quite sensitive to the form chosen for the concentration dependence of T_{gm}. In the present data−theory comparison, it was decided to use eq 14 since the parameter A in this equation is evaluated using actual experimental data points. Consequently, data−theory comparisons are carried out here for both volumetric and sorption isotherm data for the absorption−desorption cycle over the complete experimental concentration range.

Values of the parameters used to compute the predictions of the theory are presented in Table 1. The α_2 value presented in this table represents an average value over the temperature range 35−150.4 °C. Average α_2 values over different temperature ranges can be estimated using an equation presented by Zoller.[21] With the exception of the parameter χ, the property values are the same as those used in the previous data−theory comparisons.[3,5] Here, the actual value of χ estimated previously,[5] $\chi = 1.64$, was used rather than the "rounded" value $\chi = 1.75$.

The data−theory comparisons for the volumetric data are presented in Figure 1, and the data−theory comparisons for the isotherm data are presented in Figure 2. It is evident from these figures that there is good agreement between the theory and the experimental data. The greatest deviations are for the desorption isotherm at high relative pressures. It is fair to conclude that the present model, which is based on taking account of structural rearrangements of the polymer matrix, can explain hysteresis effects in the absorption−desorption cycle as well as the general nature of concentration, temperature, and polymer molecular weight effects in sorption and volumetric experiments. The key to describing the history dependence in glassy polymers is the estimation of the proportionality constant k_1. Equations 27 and 32 provide a reasonable basis for a desorption experiment, but the estimation of k_1 may be more difficult for more complicated sample histories. For the desorption process, $k_1 = 1.39$ and $k_2 = 2.43$.

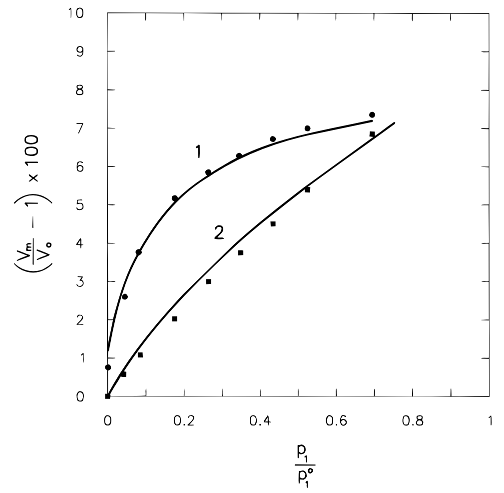

Figure 1. Comparison of theory and experiment for volumetric data at 35 °C for the polycarbonate−carbon dioxide system. Curve 1 is the prediction for desorption, and curve 2 represents the prediction for absorption. The solid circles are volumetric data[8] for desorption, and the solid squares are volumetric data[8] for absorption.

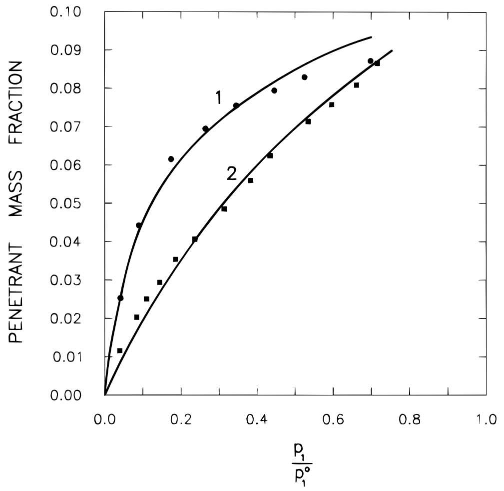

Figure 2. Comparison of theory and experiment for isotherm data at 35 °C for the polycarbonate−carbon dioxide system. Curve 1 is the prediction for the desorption isotherm, and curve 2 represents the prediction for the absorption isotherm. The solid circles are isotherm data[8] for desorption, and the solid squares are isotherm data[8] for absorption.

We conclude by summarizing some of the differences and similarities of the absorption and desorption processes in the proposed model. The differences in sample histories for the absorption and desorption cycles can conveniently be reviewed by considering a temperature−concentration diagram. For an absorption experiment, the process is started with a dry polymer at some temperature above T_{gm}, the glass transition temperature of the mixture at the desired concentration. This desired concentration is then achieved by adding penetrant at constant temperature. A conventional time scale is then used to cool the system at constant concentration to the desired temperature below T_{gm}. For a desorption experiment, the process is started with a dry polymer at temperature T, and enough penetrant is added at constant temperature to form an equilibrium polymer−penetrant mixture with $T = T_{gm}$. The desired concentration is then achieved by removing penetrant at a constant temperature T. For the absorption process, experiments at higher penetrant concentrations must of course first involve heating the sample above T_{gm} at constant concentration before additional penetrant is added at constant temperature. The cooling process is again carried out at constant concentration to the desired temperature. For the desorption process, additional desorption experiments are carried out by simply removing more penetrant at the constant temperature T.

Since the absorption experiments involve the sequential addition of penetrant and the desorption experiments involve the sequential removal of penetrant, it is reasonable to expect different volumetric and sorption behavior for nonequilibrium glassy systems. However, as noted above, data−theory comparisons show that volumetric and sorption behavior do not appear to be overly sensitive to sample preparation history when penetrant is added to a system. Hence, although the theoretical absorption sample histories are obviously different than the step-change pressure histories used in typical absorption experiments, there is generally good agreement between the predictions of the theory and experiment for absorption experiments. Desorption experiments generally involve equilibration of the sample at a high pressure and a systematic desorption to zero pressure. This history is of course similar to the theoretical sample history. In this case, there should be little error caused by the difference between experimental and theoretical histories. Consequently, it is reasonable to propose that major differences in volumetric and sorption behavior in glassy polymers will primarily depend on whether penetrant is added or removed from the polymer. Only relatively minor differences should be expected if somewhat different histories are used for an absorption experiment or a desorption experiment. It is not, in general, possible however to estimate the actual extent of these differences. Finally, we note that the different sorption and volumetric behavior exhibited by glassy polymers is caused by the concentration dependencies of the specific volume and Gibbs free energy of the polymer. These concentration dependencies simply reflect the structural rearrangements in the polymer matrix as penetrant is added.

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