2228 *Macromolecules* **1995,** *28,* 2228–2235

A Free Volume Distribution Model of Gas Sorption and Dilation in Glassy Polymers

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Received August 23, 1994; Revised Manuscript Received December 23, 1994[⊗]

ABSTRACT: A new approach is employed to model the sorption of gases in glassy polymers. The dual-mode concept that sorption occurs in both "equilibrium" (Henry's law) sites and "nonequilibrium" (Langmuir) sites is used to separate the two contributions. The Sanchez–Lacombe equation of state is applied to predict the sorption in the Henry's law region of the polymer matrix. Characteristic parameters for the polymer *liquid* are used at glassy temperatures to provide a description of sorption in a hypothetical "equilibrium" state. The additional contribution provided by sorption into the regions of excess free volume that arise from the glassy state is addressed using a modified version of an approach first proposed by Kirchheim. The excess free volume is presumed to exist in a distribution of sizes, which in turn gives rise to a distribution of sorption energies. Positron annihilation lifetime spectroscopy data are used in conjunction with *PVT* data to characterize the glassy polymer. This independent description of the glassy state is then used to calculate the Langmuir-type sorption. The resulting model uses only one adjustable parameter to provide excellent descriptions of the sorption of several gases in three polycarbonates, as well as the volume dilation caused by the sorbed gas.

1. Introduction

The challenge of modeling gas sorption and the associated volumetric changes in glassy polymers has proved to be difficult due to the nonequilibrium nature of these materials. As nonequilibrium materials, glassy polymers display a strong history dependence in their properties, and thermal, mechanical, and penetrant history can influence the sorption of gases.[1–6] The effects of gas conditioning on subsequent gas sorption and permeation have been particularly well documented.[1–5,7,8] Time-dependent aging is also known to have significant effects on permeation properties of thin polymer films and membranes.[9,10] These varying history effects dictate the need for a model of gas sorption and dilation that provides the flexibility to explicitly account for a glassy polymer's nonequilibrium morphology.

A simple model of gas sorption in glassy polymers is the well-known dual-mode model, which has been shown to describe sorption with excellent success.[11–17] The "dual modes" refer to two idealized environments in which sorption can occur. The first, termed the "Henry's law" or "dissolved" region, represents rubbery or "liquid-like" sorption, where the "equilibrium-packed" polymer chains are parted to accommodate the penetrant molecule. The second mode, the "Langmuir" region, is a consequence of the glassy state, where the pockets of excess free volume serve as "ready-made" sites for sorption, requiring less energy input to form a site for accommodation of the gas. Although the dual-mode model provides a strong conceptual framework for the mechanism of gas sorption, it is typically used as a descriptive model, employing three adjustable parameters to fit sorption isotherms at a particular temperature. Furthermore, the dual-mode model may oversimplify a more complex picture, as it only allows two distinct "modes" of sorption and neglects the concept of a distribution of sorption sites.

Other studies have applied a wide variety of models to the problem of gas sorption in glassy polymers.[18–22] While these models all show success in describing sorption isotherms, they fail to provide the flexibility to account for variations in the glass's history without prior gas/polymer mixture data. This is a serious problem in subsequent applications of such models in complex permeation processes that involve both sorption and diffusion processes. A recent approach by Kirchheim has shown promise in describing sorption in glassy polymers using the concept of a distribution of free volume.[23,24] Originally developed for hydrogen sorption in metals, Kirchheim's model assumes a Gaussian distribution of free volume hole sizes and uses Fermi–Dirac statistics to calculate the fraction of these sites that are occupied at a given gas pressure. Only an arbitrary estimate of the concentration of free volume sites is given. While Kirchheim's approach appears to be a significant breakthrough as a model that attempts to relate a detailed picture of the nonequilibrium morphology to the sorption of small molecules, there is no experimental confirmation for the free volume concentration and size distribution. Another point of concern is the premise that sorption only occurs in preexisting sites, with no provision for "Henry's law" dissolution into "equilibrium-packed" regions.

Recent studies have demonstrated that the Sanchez–Lacombe lattice–fluid (LF) equation of state can be used for the prediction of gas sorption in rubbery polymers.[25–27] This model is completely predictive, using only pure component *PVT* data and no fitting parameters. It has been suggested that the LF model also could be used to predict the dissolution of gases into the "equilibrium regions" of glassy polymers, using *PVT* data from the polymer's liquid phase.[4] This approach would predict the Henry's law sorption, as described by dual-mode theory, but would not address any additional sorption into nonequilibrium defects or microvoids.

The present paper describes a new approach to the problem of modeling gas sorption and volume dilation using the dual-mode concept that gas sorption occurs by two distinct mechanisms. The first, sorption into equilibrium regions, is predicted using the Sanchez–

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[⊗] Abstract published in *Advance ACS Abstracts,* February 15, 1995.

0024-9297/95/2228-2228$09.00/0

Lacombe LF model. The second mechanism, sorption into preexisting nonequilibrium sites, is described using a modification of the approach proposed by Kirchheim. The polymer's nonequilibrium "state" is characterized by experimental measurements of the free volume hole size distribution and concentration from positron annihilation spectroscopy and *PVT* data. By describing the two modes of sorption separately, the effects of the polymer's history-dependent morphology are isolated from what can be considered "morphology-independent" factors. The results of the model are compared to experimental sorption and volume dilation data for gases in three polycarbonates.

2. "Henry's Law" Sorption

The method for predicting gas sorption in rubbery polymers using the Sanchez–Lacombe LF equation of state has been discussed in detail previously.[27] The same approach can be used to predict gas sorption in glassy polymers, as proposed by Pope.[4] The well-known LF equation of state[28,29] is given by

$$\tilde{\varrho}^2 + \tilde{P} + \tilde{T}\left[\ln(1-\tilde{\varrho}) + \left(1 - \frac{1}{r}\right)\tilde{\varrho}\right] = 0 \tag{1}$$

Here $\tilde{\varrho}$, $\tilde{P}$, and $\tilde{T}$ are the reduced density, pressure, and temperature, respectively, of the system, while r is a parameter representing the number of lattice sites occupied by the fluid. The density, pressure, and temperature are reduced by three model parameters, ϱ^*, P^*, and T^*, which can be calculated from fits of *PVT* data or other physical quantities. The three parameters are related to r by the equation

$$\frac{RT^*\varrho^*}{P^*} = \frac{M}{r} \tag{2}$$

where M is the molecular weight of the fluid. For a glassy polymer, the three reducing parameters are fit to *PVT* data at temperatures above the glass transition. Extrapolated to lower temperatures, these parameters can be considered to represent a "hypothetical" equilibrium state of the glass.

For the case of a binary system consisting of a small molecule (subscript 1) and a high molecular weight polymer (subscript 2), the equation of state can be rearranged and written as

$$\tilde{\varrho} = 1 - \exp\left[\frac{\tilde{\varrho}^2}{\tilde{T}} - \frac{\tilde{\mathrm{P}}}{\tilde{T}} - \left(1 - \frac{\phi_1}{r_1}\right)\tilde{\varrho}\right] \tag{3}$$

where ϕ_i is the volume fraction of component i. Quantities without a subscript refer to the total binary mixture. The pressure and temperature are reduced by P^* and T^* for the binary mixture, which may be calculated from the following mixing rules using the pure component parameters:

$$P^* = \phi_1 P^*_1 + \phi_2 P^*_2 - \phi_1\phi_2({P^*_1}^{1/2} - {P^*_2}^{1/2})^2 \tag{4}$$

$$T^* = \frac{P^*}{\dfrac{\phi_1 P^*_1}{T^*_1} + \dfrac{\phi_2 P^*_2}{T^*_2}} \tag{5}$$

We will assume that the "free gas" phase is a one-component system ($\phi_1 = 1$) and write the equation of state for this phase as

$$\tilde{\varrho}_1 = 1 - \exp\left[\frac{\tilde{\varrho}_1^2}{\tilde{T}_1} - \frac{\tilde{P}_1}{\tilde{T}_1} - \left(1 - \frac{1}{r_1}\right)\tilde{\varrho}_1\right] \tag{6}$$

The condition for equilibrium between the free gas and the sorbed gas is determined by equating the chemical potentials for the gas in each phase. The equation for this condition is given, after simplification (negligible terms are omitted), by

$$\left[-\frac{\tilde{\varrho}_1}{\tilde{T}_1} + \frac{\tilde{P}_1\tilde{v}_1}{\tilde{T}_1} + (\tilde{v}_1 - 1)\ln(1-\tilde{\varrho}_1) + \frac{\ln\tilde{\varrho}_1}{r_1}\right]r_1 = \left[-\frac{\tilde{\varrho}}{\tilde{T}_1} + (\tilde{v} - 1)\ln(1-\tilde{\varrho}) + \frac{\ln\tilde{\varrho}}{r_1}\right]r_1 + \ln\phi_1 + \phi_2 + \tilde{\varrho}\chi_1\phi_2^2 \tag{7}$$

The dimensionless interaction parameter, χ_1, can be represented by

$$\chi_1 = \frac{({P^*_1}^{1/2} - {P^*_2}^{1/2})^2}{RT}\left(\frac{M_1}{\varrho^*_1}\right) \tag{8}$$

It is important to note that this simple form for the interaction parameter is intended for nonpolar mixtures and may not be appropriate for mixtures where one of the components is significantly polar. Rodgers has proposed an empirical correction for the interaction parameter using estimates of the Hansen solubility parameters.[30] The simplicity and purely predictive capability of eq 8, however, make it an attractive first approximation.

Equations 3, 6, and 7 can be solved simultaneously for a given pressure and temperature to find the value of ϕ_1 that provides equilibrium between the two phases. The volume fraction ϕ_1 is related to the weight fraction by the expression

$$\omega_1 = \frac{\phi_1}{\phi_1 + \phi_2\left(\dfrac{\varrho^*_2}{\varrho^*_1}\right)} \tag{9}$$

The weight fraction can be converted into traditional sorption units by the following expression:

$$C_\mathrm{D} = 22415\frac{\varrho_\mathrm{gl}}{M_1}\left(\frac{\omega_1}{1-\omega_1}\right) \tag{10}$$

here ϱ_gl is the density of the pure glassy polymer in g/cm^3. The "dissolved" concentration, C_D, has units of cm^3 (STP)/cm^3 of pure polymer.

3. Volume Dilation from "Henry's Law" Sorption

The volume changes caused by sorption into the "equilibrium" regions also can be described using the LF equation of state. Volume dilation is typically defined by the following expression:

$$\text{volume dilation} \equiv \frac{\Delta V}{V_0} \tag{11}$$

where ΔV is the volume change and V_0 is the volume of the unswollen *glassy* polymer (including microvoids). In terms of the LF equation of state, the contribution to the total volume dilation caused by "Henry's law" sorption can be written as

$$\frac{\Delta V_\mathrm{D}}{V_0} = \frac{\dfrac{1}{\varrho^*\tilde{\varrho}} - \dfrac{\omega_2}{\varrho^*{}_2\tilde{\varrho}_2}}{\omega_2/\varrho_\mathrm{gl}} \qquad (12)$$

where ϱ^* is given by[29]

$$\varrho^* = \varrho^*{}_1\phi_1 + \varrho^*{}_2\phi_2 \qquad (13)$$

The numerator, ΔV_D, reflects the volume changes in the "equilibrium" regions, while the denominator represents the total initial volume of the pure polymer, including free volume. Equation 12 assumes that the dilation in the equilibrium regions is fully translated into swelling of the bulk polymer. In other words, we do not allow for the possibility of an equilibrium region expanding "into" a nonequilibrium microvoid, eliminating excess free volume and reducing the total volume dilation of the bulk system. This simple assumption is consistent with past discussions of volume dilation and dual-mode theory.[16,17]

4. "Hole-Filling" Sorption

The problem of describing gas sorption and dilation of glassy polymers with a distribution of nonequilibrium free volume defects has been addressed in the recent work of Kirchheim.[23,24] Kirchheim assumes that a glassy polymer possesses a size distribution of excess free volume sites, which, as a result of their varying sizes, possess varying energies for the sorption of small molecules. The free energy of a site can be divided into two terms:[24]

$$G = G_\mathrm{el} + G_\mathrm{r} \qquad (14)$$

G_el is a contribution resulting from the elastic expansion of a site required to accommodate the penetrant, while G_r is the remaining amount. For a site that is larger than the gas molecule, no elastic straining is required to insert the molecule and $G_\mathrm{el} = 0$. For a site that is smaller than the molecule, the term G_el becomes significant. This is shown schematically in Figure 1. Using the elasticity theories of Eshelby,[31] Kirchheim states that the elastic contribution for sorption of a spherical gas of size V_g into a spherical hole of size V_h can be described by

$$G_\mathrm{el}(V_\mathrm{h}) = \frac{2}{3}\mu_\mathrm{s}\frac{(V_\mathrm{g} - V_\mathrm{h})^2}{V_\mathrm{h}} \qquad (15)$$

where μ_s is the shear modulus of the polymer. Kirchheim concedes that the continuum mechanics approach of Eshelby may be inappropriate for use with a polymeric matrix. As a first approximation, however, this provides a convenient method of estimating the energy associated with the stretching of a defect.

Kirchheim then uses Fermi–Dirac statistics to calculate the fraction of sites that are occupied at a given gas pressure

$$\text{fraction occupied} = \int_{-\infty}^{\infty}\left[\frac{n(G)}{1 + \exp\left[\dfrac{G - \mu}{RT}\right]}\right]\mathrm{d}G \qquad (16)$$

Here $n(G)$ is a probability distribution function for the energy distribution of sites and μ is the chemical potential of the gas (not to be confused with the shear modulus, μ_s). In order to convert the fraction of occupied sites to standard sorption units, the concentration of sites, N_0, must be known. The sorption is then given by

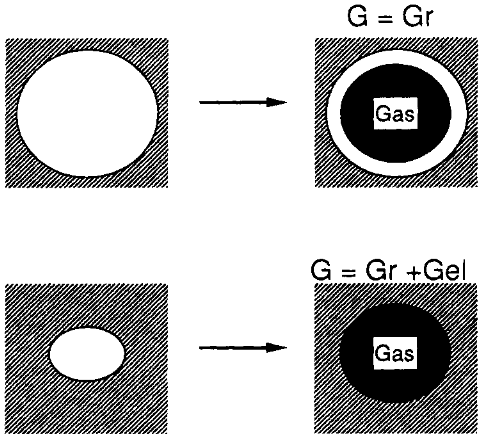

Figure 1. Schematic showing the sorption of a gas molecule into a larger hole and a smaller hole.

$$C_\mathrm{H} = N_0\int_{-\infty}^{\infty}\left[\frac{n(G)}{1 + \exp\left[\dfrac{G - \mu}{RT}\right]}\right]\mathrm{d}G \qquad (17)$$

From here, Kirchheim assumes that the free volume is distributed in a Gaussian form and fits sorption isotherms using two fitting parameters representing the Gaussian distribution. The value of N_0 is arbitrarily taken to be 6.7×10^{21} sites/cm^3 and is used for all polymers considered in his study. While Kirchheim's model provides an excellent framework for addressing a distribution of free volume, these assumptions seem to compromise its quantitative ability and generality.

If knowledge of the free volume distribution is available from external measurements, Kirchheim's model can be modified to explicitly account for this data. Equation 17 can be written in terms of a distribution of free volume hole sizes rather than a distribution of site energies such that the "hole-filling" concentration, C_H, is given by

$$C_\mathrm{H}(P) = N_0\int_0^{\infty}\frac{n(V_\mathrm{h})}{1 + \exp\left[\dfrac{G(V_\mathrm{h}) - \mu(P)}{RT}\right]}\mathrm{d}V_\mathrm{h} \qquad (18)$$

The function for the free energy of a site, $G(V_\mathrm{h})$, is given by

$$G(V_\mathrm{h}) = G_\mathrm{el}(V_\mathrm{h}) + G_\mathrm{r} \qquad (19)$$

where $G_\mathrm{el}(V_\mathrm{h})$ is the elastic contribution described by eq 15. For low sorption levels, the shear modulus (and thus $G_\mathrm{el}(V_\mathrm{h})$) is assumed to be independent of pressure. The chemical potential of the gas can be related to the pressure by the well-known relation

$$\mu = \mu_0 + RT\ln\left(\frac{f(p)}{f_0}\right) \qquad (20)$$

where $f(p)$ is the fugacity of the gas as a function of the pressure. We will take the reference chemical potential, μ_0, to be zero at the reference fugacity, $f_0 = 1$ atm. The fugacity of the gas can be calculated using the following expression:[32]

$$\ln\left(\frac{f}{p}\right) = \int_0^p \frac{z(p) - 1}{p}\,\mathrm{d}p \tag{21}$$

where $z(p)$ is function for the compressibility factor of the gas as a function of pressure.

If experimental determinations can be made for the hole size distribution function, $n(V_h)$, and the concentration of sites, N_0, the only remaining unknown parameter is G_r, which can be used as an adjustable parameter to describe the hole-filling sorption. This model is clearly intended for low sorption levels, where both the free volume distribution and the modulus of the matrix can be assumed to be independent of pressure. It is likely that both the distribution and the modulus will change as the material approaches rubbery behavior, leading to errors in the description. While one could conceivably address these issues as well, it is our intent in the present work to consider only the case where sorption levels cause negligible plasticization.

It is interesting to note that in the limiting case of an ideal gas and a polymer where all holes or microvoids are larger than the gas, $G(V_h) = G_r$ and eq 18 reduces to the form of the well-known Langmuir isotherm.

$$C_H(p) = \frac{N_0 \exp\left(-\frac{G_r}{RT}\right)p}{1 + \exp\left(-\frac{G_r}{RT}\right)p} \tag{22}$$

The parameters of this model are then related to the Langmuir capacity constant, C'_H, and the affinity constant, b, of the dual-mode equation by the following relationships:

$$C'_H = \frac{22414}{6.02 \times 10^{23}} N_0 \tag{23}$$

$$b = \exp\left(-\frac{G_r}{RT}\right) \tag{24}$$

Here C'_H has the units cm^3 STP/cm^3 while b has the units of atm^{-1}. This relationship demonstrates that Kirchheim's theory can be considered an extension of dual-model theory, as it allows for the possibility of a distribution of "intermediate Langmuir sites" that require varying degrees of swelling to accommodate the penetrant. Kirchheim's model does not include the concept of Henry's law sorption, however, suggesting the need for the LF treatment described earlier.

5. "Hole-Filling" Dilation

For sorption into smaller holes where $V_h < V_g$, a contribution to the volume dilation is expected. The elasticity theory of Eshelby[31] also addresses this issue. The volume change caused by a gas of volume V_g entering a smaller hole of volume V_h can be described by

$$\Delta V(V_h) = \gamma(V_g - V_h) \tag{25}$$

The factor γ accounts for the shear deformation that accompanies the expansion of a rigid material and is related to Poisson's ratio by

$$\gamma = 3\frac{1 - \nu}{1 + \nu} \tag{26}$$

The total volume dilation for a distribution of sites can then be described by integrating the product of $\Delta V(V_h)$ and the fractional occupancy over the distribution of small hole volumes:

$$\mathrm{Dil}(P) = N_0 \int_0^{V_g} \gamma(V_g - V_h) \times \left[\frac{n(V_h)}{1 + \exp\left[\frac{G(V_h) - \mu(P)}{RT}\right]}\right] \mathrm{d}V_h \tag{27}$$

The upper limit on the integral is the volume of the gas, V_g, as larger holes are not expected to require dilation.

6. Characterization of the Glassy State

The problem of adequately characterizing the glassy state has long been an obstacle in attempts to model sorption and transport in glassy polymers. It is expected that the excess free volume resulting from the glassy state influences the sorption and transport of gases in glassy polymers. A number of years ago, Koros and Paul suggested that the Langmuir capacity coefficient of the dual-mode equation could be related to the difference between the thermal expansion coefficients of the glassy and rubbery phases.[15] Many studies have used estimates of the fractional free volume from group contribution methods to correlate various sorption and transport properties.[2,33,34]

Until recently, however, a measure of how the free volume is distributed has been unavailable. Recent advances in the field of positron annihilation lifetime spectroscopy have provided the first experimental technique for the direct measurement of the free volume distribution in glassy polymers.[35,36] By correlating the lifetime of the orthopositronium particle with the hole radius, a probability distribution function (PDF) such as that required by eqs 18 and 27 can be determined. The PDF is first calculated in terms of the hole radius and defined such that the fraction of holes with radius between r and $\mathrm{d}r$ is given by $n'(r)\,\mathrm{d}r$. Approximating the holes to be spherical, the hole radius PDF, $n'(r)$, can then be converted to the volume PDF, $n(V_h)$, by the following equation:[35]

$$n(V_h) = \frac{n'(r)}{4\pi r^2} \tag{28}$$

Here r is the radius of the spherical hole.

In order to calculate the site density, N_0, a measure of the total free volume contributed by these sites must also be known. The fractional free volume (FFV) usually reported for glassy polymers is that which has been calculated using the group contribution method of Bondi.[37] This measure considers all free volume in the polymer, including volume "swept out" by thermal motions of the chains in the "equilibrium" regions, as well as nonequilibrium defects resulting from the glassy state. Since we are concerned with the free volume associated with "holes" or preexisting sorption sites, the FFV from Bondi's method seems to be inappropriate for our use.

Instead, data from pressure–volume–temperature (PVT) measurements can be used to determine the "excess" fractional free volume (EFFV) associated with the nonequilibrium state. It has been found that the density of polymer liquids is linear with temperature over a wide temperature range.[38] With this knowledge, the linear function for the density of the liquid polymer,

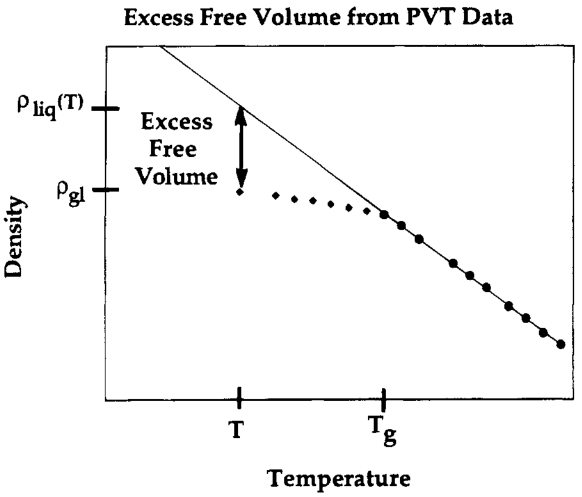

Figure 2. Schematic showing the definition of excess free volume in a glassy polymer at temperature *T*.

$\varrho_{\text{liq}}(T)$ can be extrapolated into the glassy temperature range to provide a measure of the hypothetical "equilibrium" density that a glassy polymer will eventually reach if allowed to age for an infinite period of time. The EFFV can then be calculated by

$$\text{EFFV}(T) = 1 - \frac{\varrho_{\text{gl}}}{\varrho_{\text{liq}}(T)} \tag{29}$$

where ϱ_{gl} is the density of the glass at temperature *T*. Figure 2 shows this interpretation of excess free volume, using a plot of density versus temperature for a typical glassy polymer. The site density can then be calculated using the following equation:

$$N_0 = \frac{\text{EFFV}}{\int_0^\infty V_{\text{h}} n(V_{\text{h}})\,\mathrm{d}V_{\text{h}}} \tag{30}$$

One can thus "characterize" a particular glassy state by two measurements: the free volume PDF and the temperature-dependent density of the glass (which leads to the EFFV). Alternate histories for a glassy polymer can be characterized by *independent* measurements of these two quantities, allowing one to separate the effects of the nonequilibrium morphology from the thermodynamics of gas sorption. One facet of the glassy morphology that is not addressed by this characterization is the shape of the free volume sites. We are limited to the assumption of a spherical geometry, which may or may not be an accurate approximation for the shape of the sites.

It should be noted that we do not require that the free volume exists in a static, fixed position. We expect that density fluctuations will cause a slow migration of these holes through the matrix, as well as fluctuations in an individual hole's size. Over long time scales, these motions may cause significant changes in the polymer morphology, leading to the observed aging behavior in glassy materials. Over experimental time scales, however, we assume that the overall size distribution and hole density remain constant, despite fluctuations in the individual holes.

7. Sorption and Dilation Isotherms for Various Gases in Three Polycarbonates

Using the theory described above, isotherms were calculated for the sorption and volume dilation of various gases in three polycarbonates: Bisphenol-A polycarbonate (PC), tetramethylpolycarbonate (TMPC), and hexafluoropolycarbonate (HFPC).

Table 1. Values of the LF Equation of State Reducing Parameters for Gases and Polymers

component	T^*, K	P^*, atm	ϱ^*, g/cm^3	*r*	ref
CO_2	309	5666	1.505	6.54	39
CH_4	199.2	2493	0.4846	5.05	27
N_2	129	1933	0.9452	5.41	27
C_2H_4	277.5	3357	0.6682	6.19	27
PC	768.2	5324	1.2743	∞	40[a]
TMPC	761.6	4407	1.1739	∞	41[a]
HFPC	716.5	4403	1.6184	∞	41[a]

[a] Nonlinear least squares fit performed on raw *PVT* data from these sources.

Table 2. Volumetric Quantities for Polycarbonates

polymer	ϱ_{gl}, g/cm^3	$\varrho_{\text{liq}}(T)$, g/cm^3	EFFV at 35 °C	data source
PC	1.20	$1.4683 - 6.901 \times 10^{-4}T$ (K)	0.044	40
TMPC	1.083	$1.3538 - 6.777 \times 10^{-4}T$ (K)	0.057	41
HFPC	1.478	$1.9006 - 10.642 \times 10^{-4}T$ (K)	0.060	41

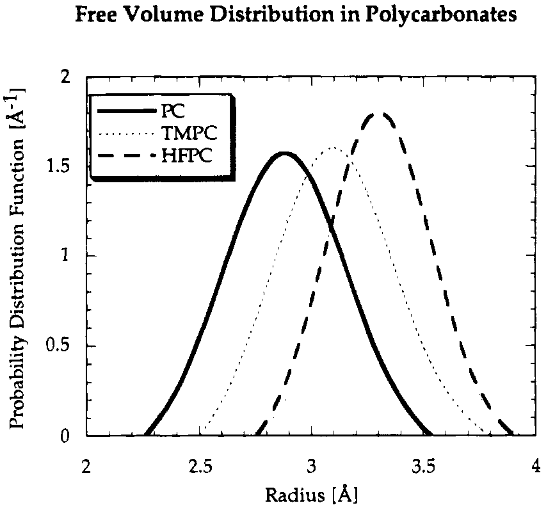

Figure 3. Probability distribution function for the hole radii in three polycarbonates at 35 °C as determined by positron annihilation lifetime spectroscopy.[42]

Values for the LF reducing parameters for the polymers and gases considered are shown in Table 1. With the exception of carbon dioxide, the gas parameters were all taken from the study by Pope et al.[27] The CO_2 parameters from the Pope study were fit at the triple point and were found to provide poorer predictions than those of Panayiotou and Sanchez,[39] which were fit over a wider range of data. The polymer parameters were calculated from a nonlinear least-squares fit of *PVT* data[40,41] over a pressure range of 0–50 MPa. The temperature range for these fits spanned from roughly 10–15 °C above the glass transition temperature to roughly 250 °C for PC and 285 °C for TMPC and HFPC. The data used to calculate the EFFV for the three polymers are shown in Table 2. Experimental measurements of the hole radius distribution were available for the three polymers and are shown in Figure 3.[42] It was found that the PDF could be fit using the following form:

$$n'(r) = \frac{1}{m_1 \pi^{1/2}} \exp\left[-\frac{(r - m_2)^2}{m_1^{\,2}}\right] + m_3 + m_4 r + m_5 r^2 \tag{31}$$

Table 3. Hole Radius Distribution Parameters for Polycarbonates

	PC	TMPC	HFPC
m_1	0.3739	0.3680	0.3238
m_2	2.881	3.091	3.300
m_3	−3.029	−3.675	−4.701
m_4	2.111	2.320	2.816
m_5	−0.360	−0.359	−0.416
eff range [Å]	2.21−3.55	2.50−3.80	2.73−3.92
vol range [Å^3]	45−187	65−230	85−252

Table 4. Values of G_r [kJ/mol] for Polymer/Gas Pairs

	gas			
polymer	CO_2	CH_4	N_2	C_2H_4
PC	7.1	9.3	13.8	5.5
TMPC	2.2	6.5	10.4	
HFPC	2.8	7.1	9.6	

where m_1, m_2, m_3, m_4, and m_5 are constants. The first term in the equation represents a Gaussian distribution, which by itself was found to provide fair fits of the experimental data. The additional polynomial terms were added to improve the description of the hole distribution. The values of the five constants for each polymer are tabulated in Table 3. The effective range for the distribution is also shown in terms of both radius and spherical volume. The number of holes outside this range are considered to be negligible. The integrations in eqs 18 and 27 can be performed over these ranges rather than using the infinite limits. It should be noted that while a Gaussian form provides a reasonable fit of the hole *radius* distribution, it will not provide a good description of the hole *volume* distribution as the volume distribution becomes skewed by eq 28. This suggests that Kirchheim's assumption of a Gaussian volume distribution may be inappropriate.

Using eq 30, the site density, N_0, now can be calculated. For PC, TMPC, and HFPC, the site densities (in sites/cm^3) were 4.28×10^{20}, 4.44×10^{20}, and 3.91×10^{20}, respectively. For HFPC, virtually all the holes are larger than small gas molecules and thus the limiting case described earlier is valid. Using eq 23, one can predict a Langmuir capacity constant of 14.6 cm^3 STP/cm^3. Dual-mode fits for experimental measurements of carbon dioxide and methane sorption yield values of 13.7 and 12.8 cm^3 STP/cm^3, respectively.

Isotherms were then fit to experimental sorption data, using G_r as the *only* fitting parameter. The sorption prediction is the sum of the contributions from eqs 10 and 18. The values for the gas volume, V_g, were taken from the measurements of the partial molar volume in silicone rubber.[27] For carbon dioxide, methane, nitrogen, and ethylene, these values were 76.6, 86.7, 82.6, and 96.8 Å^3, respectively. G_r was adjusted to provide the best fits of the data, particularly in the low-pressure region where the effects of hole-filling sorption are more evident. The values of G_r that provide the best fits are listed in Table 4. Again, the values of G_r for HFPC can be used to investigate the limiting case where all holes are larger than the gas. Using eq 24, G_r can be related to the Langmuir affinity constant, b, from dual-mode fits. Table 5 compares the results from fits of experimental data to the value calculated with eq 24.

Table 5. Comparison of the Predicted Langmuir Affinity Constant with Experimental Values for the Sorption of Carbon Dioxide and Methane in HFPC

	Langmuir affinity constant, b [atm^{-1}]	
gas	exptl (dual mode)	calcd (eq 24)
carbon dioxide	0.391	0.335
methane	0.070	0.062

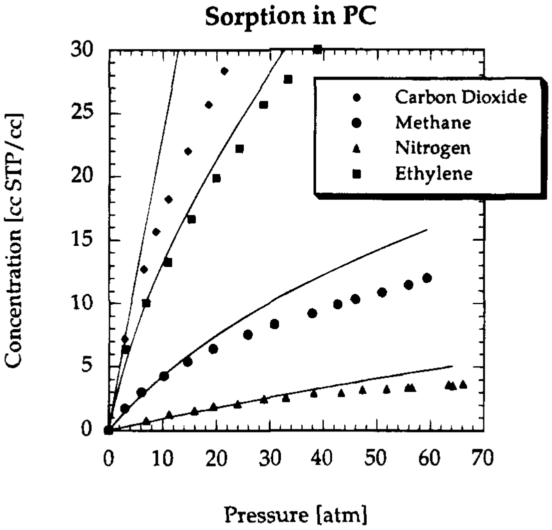

Figure 4. Sorption of various gases in PC at 35 °C. The points represent experimental data while the lines represent the theory.

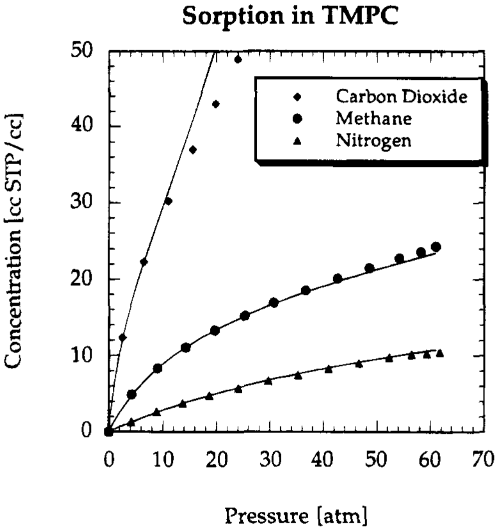

Figure 5. Sorption of various gases in TMPC at 35 °C. The points represent experimental data while the lines represent the theory.

The results of the theoretical sorption descriptions are shown in Figures 4−6. The solid lines represent the theory, while the points are taken from experimental data.[1] Ethylene sorption data were not available for TMPC and HFPC. Good descriptions were obtained for the sorption isotherms, particularly in the cases of methane and nitrogen in TMPC and HFPC, where both the shape and magnitude of the isotherms are well predicted. The poorest descriptions were obtained for sorption in PC, as the curvatures of the isotherms do not seem to match those of the experiments. For all four gases, the isotherms do not seem to "saturate out" soon enough, suggesting that the value of N_0 was overestimated, by errors in the measurement either of the distribution or of the EFFV. To compensate for an overestimation of N_0, the values for G_r are likely overestimated as well, as G_r was adjusted to provide the correct magnitude of the sorption isotherm.

The isotherms for CO_2 sorption were found to be slightly overpredicted for all three polymers. This is particularly evident in the higher pressure range where

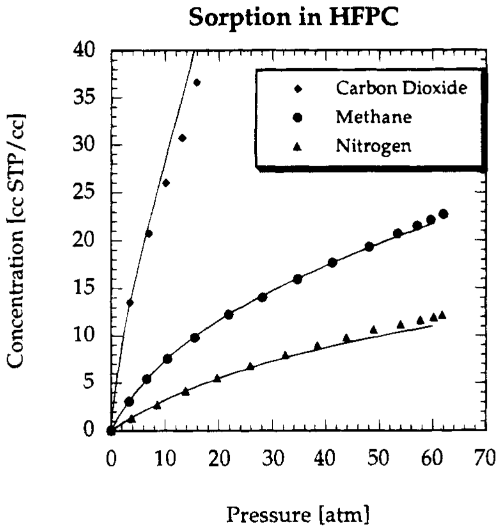

Figure 6. Sorption of various gases in HFPC at 35 °C. The points represent experimental data while the lines represent the theory.

the Henry's law contribution begins to dominate: the slope of the predicted isotherm is higher than that of the experimental isotherm in all three cases. This suggests that the main source of error lies in the LF prediction of the Henry's law sorption. It is likely that this is caused by errors in the estimate of the interaction parameter made from eq 8. Mixing between the carbonyl groups in the polycarbonates and the quadrupolar carbon dioxide may not be adequately described by this simple form. This effect seems to be exaggerated in the case of PC, where the density of carbonyl groups is the highest. Errors at higher gas concentrations may also be explained by plasticization effects, for the modulus and free volume distribution may not remain constant as the concentration increases. Overall, however, the model is surprisingly successful, considering that only one adjustable parameter is employed.

Using the values of G_r found for the sorption isotherms, along with the weight fractions calculated from eq 9, the volume dilation is predicted for the same gas/polymer mixtures. The volume dilation is taken as the sum of the contributions from eqs 12 and 27; the results are shown in Figures 7–9. Again, the theory provides a good representation of the experimental data. As the dilation is expected to be dominated by the Henry's law contribution, the results of the LF prediction become more evident. For all three polymers the theory slightly overpredicts for CO_2, slightly underpredicts for nitrogen, and provides a good estimate for the magnitude of methane dilation. The dilation of PC with ethylene also shows good agreement with the experimental data. The overprediction of the CO_2 dilation is consistent with the argument that the prediction of χ from eq 8 is slightly in error. Again, the overprediction is most pronounced for the PC/CO_2 mixture, where the largest polar effects are expected. One unfortunate observation is that the model predicts very little curvature in the shape of the isotherms. This is particularly problematic in the case of methane, which clearly does not display linear dilation in any of the polycarbonates. This deficiency suggests that some additional mechanism is neglected in the treatment of the volume changes. In general, however, the description of the volume dilation is remarkable, considering that it is primarily predicted from the LF equation of state, a complete *prediction* from pure component properties.

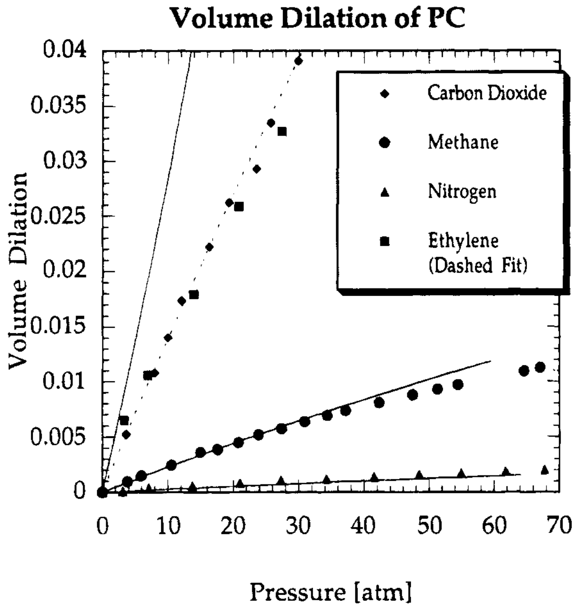

Figure 7. Dilation of PC by several gases at 35 °C. The points represent experimental data while the lines represent the prediction from theory. The dashed line is the prediction for ethylene, while the highest solid line is the prediction for carbon dioxide.

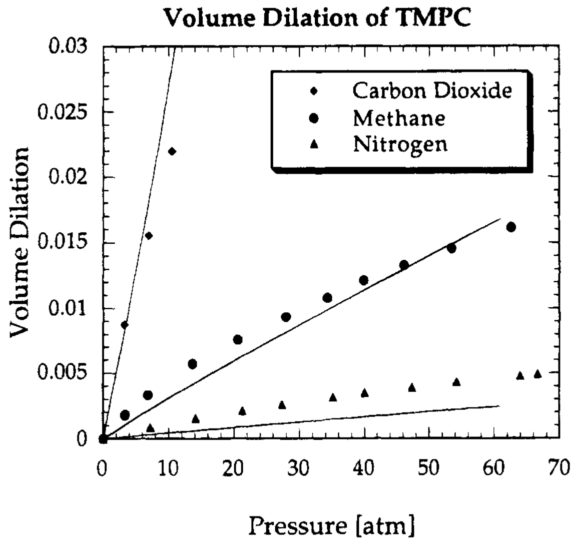

Figure 8. Dilation of TMPC by several gases at 35 °C. The points represent experimental data while the lines represent the prediction from theory.

8. Conclusion

The model described in this study unites concepts from dual-mode theory, the lattice–fluid equation of state, and the hole-filling model of Kirchheim, with experimental characterizations of the glassy state. Using only one fitting parameter (the morphology-independent free energy of sorption, G_r), experimental sorption and dilation isotherms were fit with good success. This study has considered only predictions from pure component data for the value of the interaction parameter χ. If we allow this to be a second fitting parameter, even better descriptions of sorption and dilation can be obtained.

The model's most important feature is its ability to relate an independent description of the glassy state to the problem of gas sorption and dilation. By isolating the glassy state description from the "equilibrium" parameters of the model, we gain the flexibility to

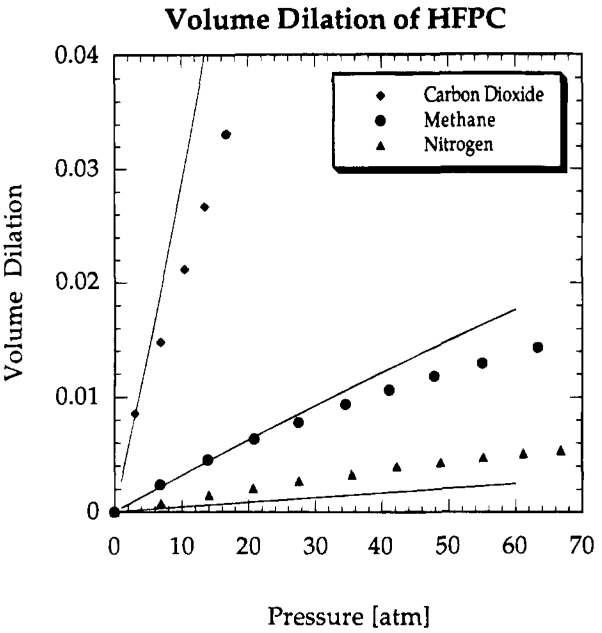

Figure 9. Dilation of HFPC by several gases at 35 °C. The points represent experimental data while the lines represent the prediction from theory.

predict sorption in glasses with various histories, assuming that a "characterization" of the history is available. Our "characterization" in this study was a measure of the hole size distribution and a measurement of the excess fractional free volume through *PVT* measurements of the density in the liquid phase and of the glass in question. The density of the liquid phase can be considered an equilibrium parameter as it should be independent of the glassy morphology. Once appropriate values for the equilibrium parameters G_r and χ are determined for a particular glass history, they should be directly applicable to the *prediction* of sorption and dilation in glassy polymers of any history.

Acknowledgment. The authors would like to thank the Separations Research Program for their support of this research. We also wish to thank Dr. Y. C. Yean for providing the positron annihilation spectroscopy data used in this study.

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MA945007D