A Lattice-Based Activity Coefficient Model for Gas Sorption in Glassy Polymers

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ABSTRACT: The glassy polymer lattice sorption model (GPLSM) is a lattice-based activity coefficient model that has been developed for gas sorption in glassy polymers. The model recognizes the presence of holes on the lattice and determines how the number of holes changes by taking into account swelling due to penetrant gas molecules. The GPLSM equation has a composition-dependent energy term similar to that in the Flory–Huggins theory and an entropic term based on the mixing of gas molecules and holes. The utilization of sorptive dilation data for the determination of the number of holes gives a physically realistic interpretation of the local free volume in a glassy polymer. A good representation of the experimental data is obtained for the carbon dioxide– and methane–polycarbonate systems.

Introduction

The most widely used model to correlate gas sorption data in glassy polymers at low to moderate pressures is the dual-mode sorption model.[1-3] This model assumes that two distinct populations of penetrant molecules exist within the glassy polymer, one in which molecules are sorbed by an ordinary dissolution mechanism (the *dissolved* or *Henry's law* population) and one in which molecules reside in preexisting gaps frozen into the glassy polymer as it was cooled through the glass transition temperature (the *hole* or *Langmuir* population). In addition, local equilibrium is assumed to exist between the two populations of penetrant molecules. The model is given by

$$C = k_{\mathrm{D}}p + \frac{C_{\mathrm{H}}'bp}{1 + bp} \qquad (1)$$

where C is the concentration of gas in the polymer, k_{D} is the Henry's law solubility coefficient, p is the gas pressure, C_{H}' is the Langmuir capacity of the glassy polymer, and b is the Langmuir affinity constant. This model has found widespread use in modeling gas sorption in glassy polymers and seems to explain many of the phenomena associated with glassy polymer thermodynamics. Although physical interpretations have been given to the parameters of this model, it is based on phenomenological observations of early investigators[1-3] and as such is an empirical model.

Another empirical model is the gas–polymer–matrix model:[4]

$$C = \sigma_0 p e^{-\alpha C} \qquad (2)$$

where σ_0 is the solubility coefficient at infinite dilution and α is a constant describing the effect of gas–polymer interactions on changes in the solubility. This model assumes that the gas molecules exist in the glass as a single population and that the observed nonlinearities are due to gas–polymer interactions. Although this model fits the data well, the parameters cannot be correlated in a meaningful way,[5] and thus the model has found limited use.

Relatively little work has been done in the development of theoretically based models for glassy polymer–gas mixtures. Recently, Wissinger and Paulaitis[6] applied the Panayiotou and Vera equation of state,[7] a lattice-based model originally developed for liquid polymers, to gas sorption in rubbery polymers and then extended it into the glassy region. This model assumes the existence of holes on the lattice and is based on a quasi-chemical approximation that accounts for nonrandom mixing. This equation has two molecular ordering parameters, one of which accounts for the number of holes in the glassy polymer and one that describes the number of contacts between segments.[7] Wissinger and Paulaitis fit this model to the rubbery region, fixed the number of holes in the system to the value obtained at the glass transition temperature, and extrapolated the model into the glassy region of the sorption isotherm. This approach produced a reasonable fit of the sorption data over an extensive range of pressures and also provided a quantitative estimate of polymer swelling. However, in order to better fit the curvature of the sorption isotherm for a polymer well below its glass transition temperature, the number of holes in the glassy polymer must be allowed to change with sorbed gas in the polymer. This forms the basis for the development of the glassy polymer lattice sorption model (GPLSM).

Model Development

Previous theoretical work on gas sorption in glassy polymers centered on applying models that had been developed for liquid systems to polymers in the glassy state.[6] The present work describes the development of a lattice-based activity coefficient model specifically for the case of gas sorption in glassy polymers.

Since a glassy polymer is not in thermodynamic equilibrium, an activity model was chosen rather than an equation of state. An equation of state is not appropriate because, for a glassy polymer, a unique value for the volume of the pure polymer cannot be calculated from the pressure and temperature. However, in an activity model, once a volume is specified, the activity of the gas in the polymer can be calculated.

A certain amount of unrelaxed free volume is frozen into a glassy polymer as it is cooled through the glass transition temperature. The relaxation is slow enough below T_g to allow the polymer to be modeled as a quasi-equilibrium system. The amount of unrelaxed free volume existing in the polymer glass is a function of the thermal history of the polymer. Thus, the volume of the glassy polymer can be considered to be a molecular ordering parameter for the system.

Similar to the Panayiotou and Vera equation of state[7] as well as that of Sanchez and Lacombe,[8] GPLSM takes

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into account the presence of holes on a lattice. In GPLSM, these holes consist of the microvoidal free volume that exists below the glass transition temperature of the polymer in addition to the free volume normally associated with the liquid state. Due to the fact that the relaxation process is slow in a polymer below its T_g, the polymer segments are assumed to be completely immobile at temperatures significantly below the glass transition temperature of the gas–polymer mixture. This assumption is similar to that made by Gibbs and DiMarzio[9] in their lattice model describing the glass transition of polymers. As a consequence of this, the polymer segments do not contribute to the entropy of mixing, which is due entirely to the combinatorial mixing of holes and gas molecules.

By definition, the activity of a gas in a mixture is related to the free energy of mixing by the expression

$$kT \ln a_g = \left(\frac{\partial \Delta G_{\text{mix}}}{\partial N_g}\right)_{P_T,T,N_r} \tag{3}$$

where a_g is the activity of the gas in the glassy polymer, N_g is the number of gas molecules, ΔG_{mix} is the free energy of mixing for the process, k is the Boltzmann constant, T is the absolute temperature of the system, P_T is the total system pressure, and N_r is the number of polymer segments in the system. For any mixing process, ΔG_{mix} is given by the expression

$$\Delta G_{\text{mix}} = \Delta U_{\text{mix}} + P_T \Delta V_{\text{mix}} - T\Delta S_{\text{mix}} \tag{4}$$

where, for the case of gas sorption in glassy polymers, ΔU_{mix} is associated with the energy of placing gas molecules on the lattice; ΔV_{mix} accounts for the nonideal swelling in glassy polymers; and ΔS_{mix} describes the combinatorial mixing of holes and gas molecules.

ΔU_{mix} is given by the expression

$$\Delta U_{\text{mix}} = U_{\text{mixture}} - U_g^{\text{pure}} - U_r^{\text{pure}} \tag{5}$$

where U_{mixture} is the internal energy of the mixture, U_g^{pure} is the internal energy of the pure gas, and U_r^{pure} is the internal energy of the pure polymer segments. When the internal energy of the mixture depends only on nearest-neighbor interactions, it is given by[8]

$$U_{\text{mixture}} = \frac{z}{2}\sum_{i=1}^{2}\sum_{j=1}^{2} N_i p_{ij} \Gamma_{ij} \tag{6}$$

where z is the coordination number, N_i is the number of molecules of component i in the mixture, Γ_{ij} is the energy per interacting pair, and p_{ij} is the probability that component i at a particular lattice site interacts with j. Using a mean field approximation, p_{ij} becomes the fraction of coordination sites around i occupied by j. The summation in eq 6 is performed over the two species involved in the mixture: gas molecules (g) and polymer segments (r). However, not all of the lattice sites are occupied. If a lattice site is empty, it is said to contain a hole (h). Holes are not treated as components in the system but are accounted for in the expression for the probability that a lattice site is occupied, which is given by

$$p_{ij} = \frac{N_j}{N_g + N_r + N_h} \tag{7}$$

Setting the energy cross-interaction terms equal to one another, $\Gamma_{rg} = \Gamma_{gr}$ and $\Gamma_{hg} = \Gamma_{gh} = 0$, the mean field expression for the internal energy of the mixture becomes

$$U_{\text{mixture}} = \frac{z}{2}\left(\frac{N_g^{\,2}}{N_T}\Gamma_{gg} + 2\frac{N_r N_g}{N_T}\Gamma_{rg} + N_r\frac{N_{r,\text{nc}}}{N_T}\Gamma_{rr}\right) \tag{8}$$

where $N_{r,\text{nc}}/N_T$ is the fraction of sites coordinated around a polymer segment that form noncovalent interactions with the segment and $N_T = N_g + N_h + N_r$. N_r refers to all polymer segments, covalently and noncovalently interacting with one another, unless otherwise designated.

The pure polymer contains holes and polymer segments. The internal energy of the pure polymer is given by

$$U_r^{\text{pure}} = \frac{z}{2} N_r p_{rj} \Gamma_{rj} \tag{9}$$

where the probability that a coordination site is occupied by a polymer segment is given by

$$p_{rj} = N_{r,\text{nc}}/N_T^{\,0} \tag{10}$$

where $N_T^{\,0} = N_h^{\,0} + N_r$.

A pure gas in its hypothetical liquid state is assumed to contain holes and gas molecules. The expression for the internal energy of the pure gas is obtained by replacing the subscript r with g in eq 9. Applying the same assumptions used for the pure polymer to the case of a pure gas produces the expression for the internal energy of the pure gas:

$$U_g^{\text{pure}} = \frac{z}{2} N_g \frac{N_g'}{N_T'} \Gamma_{gg} \tag{11}$$

where N_g'/N_T' is the fraction of sites in the pure gas actually occupied by gas molecules and $N_T' = N_g' + N_h'$.

Substitution of eqs 8, 9, and 11 into eq 5 gives the following expression for the internal energy of mixing for the process:

$$\Delta U_{\text{mix}} = \frac{z}{2}\frac{N_r N_g}{N_T}(2\Gamma_{rg} - \alpha\Gamma_{gg} - \beta\Gamma_{rr}) \tag{12}$$

where

$$\alpha = \frac{N_g'}{N_T'}\left(\frac{N_T - N_T'}{N_r}\right) \tag{13}$$

and

$$\beta = \frac{N_{r,\text{nc}}}{N_T^{\,0}}\left(\frac{N_T - N_T^{\,0}}{N_g}\right) \tag{14}$$

Physically, α and β account for nonideal changes in the number of holes upon mixing gas and polymer.

A term describing the change in volume upon mixing is included since there is experimental evidence of a negative volume change upon mixing penetrant gas molecules with a glassy polymer.[10–13] The following expression describes the nonideal change in volume upon addition of penetrant molecules:

$$\Delta V_{\text{mix}} = V_{\text{mixture}} - V_r^{\text{pure}} - V_g^{\text{pure}} \tag{15}$$

where V_{mixture} is the volume of the penetrant–polymer mixture, V_r^{pure} is the volume of the pure polymer, and V_g^{pure} is the volume of the pure gas. Assuming the volume of a lattice site, V_s, to be constant, the mixture volume is obtained by multiplying the volume of a lattice site by the total number of sites occupied by gas molecules, holes, and polymer segments in the mixture. The volumes of the pure polymer and pure gas are obtained in a similar manner. Thus, the volume change upon mixing gas molecules with a glassy polymer is given by the following expression:

$$\Delta V_{\text{mixing}} = V_s(N_T - N_T^{\,0} - N_T') \tag{16}$$

The entropy of mixing is given by the following expression:

$$\Delta S_{\text{mixing}} = S_{\text{mixture}} - S_r^{\text{pure}} - S_g^{\text{pure}} \tag{17}$$

At temperatures below the glass transition temperature of the mixture, the polymer segments are assumed to be completely immobile[9] and thus the polymer does not contribute to the entropy of mixing. Assuming only combinatorial entropy, the entropy of mixing term describes the ideal mixing of gas molecules and holes. Applying the Boltzmann expression for combinatorial entropy, the entropy of the mixture is described by the following expression:

$$S_{\text{mixture}} = -k\left(N_g \ln \frac{N_g}{N_g + N_h} + N_h \ln \frac{N_h}{N_g + N_h}\right) \tag{18}$$

Assuming that the pure gas consists of holes and gas molecules, the entropy of the pure gas is described by the expression above, in which the N_h and N_g refer to the number of holes and gas molecules in the pure gas, respectively. Since the polymer segments are assumed to be immobile, there is no contribution from the pure polymer. Thus, the entropy of mixing is given by

$$\Delta S_{\text{mixing}} = k\left(N_g' \ln \frac{N_g'}{N_g' + N_h'} + N_h' \ln \frac{N_h'}{N_g' + N_h'} - N_g \ln \frac{N_g}{N_g + N_h} - N_h \ln \frac{N_h}{N_g + N_h}\right) \tag{19}$$

Substitution of eqs 12, 16, and 19 into eq 4 and dividing by kT yield the complete expression for the free energy of mixing for the process:

$$\frac{\Delta G_{\text{mix}}}{kT} = -N_g \ln \frac{N_g}{N_g + N_h} - N_h \ln \frac{N_h}{N_g + N_h} + N_g' \ln \frac{N_g'}{N_g' + N_h'} + N_h' \ln \frac{N_h'}{N_g' + N_h'} + \psi \frac{N_g N_r}{N_g + N_r + N_h} + \frac{PV_s}{kT}(N_T - N_T^0 - N_T') \tag{20}$$

where

$$\psi = \frac{z}{kT}(2\Gamma_{rg} - \alpha\Gamma_{gg} - \beta\Gamma_{rr}) \tag{21}$$

Differentiation of eq 20 with respect to N_g at constant total pressure, temperature, and N_r (eq 3) leads to a rather cumbersome expression for the activity of the gas in the glassy polymer. This expression is given in the Appendix.

Calculation of an activity coefficient from the activity requires that a reference state be chosen for the system. In this study, the activity of the gas in the reference state is chosen to be the number fraction of gas molecules on a gas- and hole-free basis, N_g/N_r. Subtraction of the natural logarithm of this reference state from the natural logarithm of the activity leads to the expression for the activity coefficient, γ, which is also given in the Appendix. This activity coefficient was asymmetrically normalized such that it approaches unity for the pure polymer by dividing γ by γ^∞, the infinite-dilution activity coefficient. The resulting expression for phase equilibria is

$$f_g = \frac{N_g}{N_r}\gamma^* H \tag{22}$$

where f_g is the fugacity of the gas, γ^* is the *asymmetrically* normalized activity coefficient (see Appendix), and H is the Henry's law constant.

GPLSM is similar in form to other familiar equations appearing in the literature. If holes are not included, the α and β modifiers in the ΔU_{mix} expression reduce to unity and the expression for the internal energy reduces exactly to that of the familiar Flory–Huggins equation. However, in contrast to Flory–Huggins theory, in the absence of holes, the entropy expression drops out of the equation. Also, Flory–Huggins theory assumes an ideal volume of mixing. It is also interesting to note that if GPLSM is cast into an equation of state, the energy term is identical with that of Sanchez and Lacombe.[8] GPLSM differs from the Sanchez–Lacombe equation in that (1) the GPLSM entropy term does not include contributions from the mobility of polymer segments, (2) GPLSM includes a ΔV_{mix} term, and (3) N_h in GPLSM is a history- and concentration-dependent molecular ordering parameter specific to each glassy polymer–gas system.

Application of the Model

Most of the parameters in GPLSM are fixed by the system being examined or fixed for all systems. The coordination number, z, is set equal to 10. The number of segments forming noncovalent polymer–polymer interactions is determined from the following equation:

$$N_{r,nc} = fN_r \tag{23}$$

where f, the fraction of these segments, is calculated from[8]

$$f = \frac{z-2}{z} + \frac{2}{zr} \tag{24}$$

In eq 24, r is the number of lattice sites occupied by polymer segments in a polymer molecule. This is not the same as the number of repeat units in a polymer molecule or the degree of polymerization since the size of a lattice site is based on the size of the penetrant. Hence the value of f for large r and a z of 10 is 0.8.

The volume of a lattice site, V_s, could be obtained from the Bondi volume[14] of the penetrant gas molecule, but in this study, since an equation-of-state-determined interaction energy will be used for the pure gas, the corresponding hard-core volume of the gas is used to determine V_s. The fraction of sites in the pure gas actually occupied by gas molecules is calculated by the following expression:

$$\frac{N_g'}{N_T'} = \frac{\bar{V}_s}{\bar{V}'} \tag{25}$$

where $\bar{V}'$ is the *hypothetical liquid molar volume* of the pure gas and $\bar{V}_s$ is the *molar* volume of a lattice site.

The most important parameter in the model is the number of holes in the polymer, N_h. The number of holes initially present as well as how N_h changes as a function of pressure (or N_g) must be determined. The initial number of holes is related to the unoccupied free volume of the polymer. It is determined by subtracting the close-packed volume of the polymer, obtained by extrapolating the equilibrium volume of the liquid through the glass transition temperature to absolute zero, from the volume of the glass at the system temperature (see Figure 1). It is described by the following equation:

$$\frac{N_h^0}{N_r} = \frac{\hat{V}_T - \hat{V}_{cp}}{\hat{V}_{cp}} \tag{26}$$

where $\hat{V}_T$ is the specific volume of the pure glassy polymer at temperature T and $\hat{V}_{cp}$ is the specific close-packed volume of the polymer.

The specific volume of the polymer at the temperature of interest is determined from its specific volume at the glass transition temperature, $\hat{V}_{Tg}$, by the following equation:

$$\hat{V}_T = \hat{V}_{Tg} - \alpha_g(T_g - T) \tag{27}$$

where T is the system temperature and α_g is the thermal expansion coefficient of the glass. The close-packed volume is obtained by using α_l for the equilibrium liquid

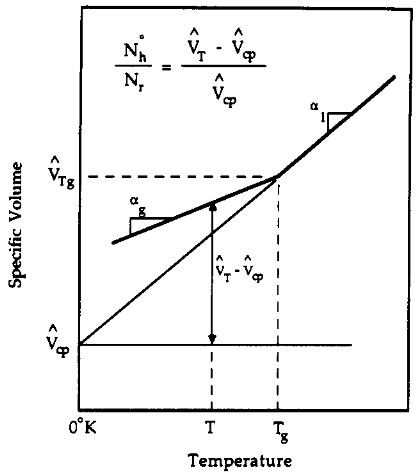

Figure 1. Determination of the initial number of holes, N_h^0, from the unoccupied free volume, $\hat{V}_T - \hat{V}_{cp}$.

with a system temperature of 0 K in the above equation.

The manner in which the number of holes in the polymer changes as a function of pressure is determined by using actual sorptive dilation data $(\Delta V/V_0)_T$ as a function of pressure. The number of holes in the polymer at a given system temperature and penetrant gas pressure is given by the following expression:

$$\frac{N_h}{N_r} = \frac{N_h^0}{N_r} + \frac{\Delta\hat{V}}{\hat{V}_{cp}} - \frac{N_g}{N_r} \tag{28}$$

where

$$\Delta\hat{V} = \hat{V}_T\left(\frac{\Delta V}{V_0}\right)_T \tag{29}$$

The number of gas molecules sorbed on a gas- and hole-free basis, N_g/N_r, is determined through the phase equilibria relationship (eq 22). By equating the fugacity of the gas in the glassy polymer to the fugacity of the pure gas (assuming nonvolatile polymer), which in this study is determined by the Peng–Robinson equation of state,[15] N_g/N_r is obtained.

Upon differentiation of ΔG_{mixing} with respect to N_g to obtain the activity expression, the derivative $\partial N_h/\partial N_g$ arises from the differentiation of N_T (see Appendix). This derivative represents the change in the number of holes in the mixture as gas is sorbed into the glassy polymer. This is related to sorptive dilation data by differentiation of eq 28 through the following relationship:

$$\frac{\partial N_h}{\partial N_g} = \frac{N_r}{\hat{V}_{cp}}\left(\frac{\partial \Delta\hat{V}}{\partial N_g}\right) - 1 \tag{30}$$

where $\partial\Delta\hat{V}/\partial N_g$ is the change in swelling upon sorption of gas molecules. This is related to the experimentally measured sorptive dilation data through the following relationship:

$$\frac{\partial \Delta\hat{V}}{\partial N_g} = \frac{\partial \Delta\hat{V}}{\partial P}\frac{\partial P}{\partial N_g} \tag{31}$$

where $\partial\Delta\hat{V}/\partial P$ is the derivative of the dilation data with respect to pressure. $\partial P/\partial N_g$ remains in the final expression for the activity of the gas in the polymer, and thus the expression must be solved as a differential equation (see Appendix).

Four parameters remain in the model, the Henry's law constant, H, and the three interaction energies, Γ_{rr}, Γ_{rg}, and Γ_{gg}, which correspond to segment–segment, segment–gas, and gas–gas interactions, respectively. The Henry's law constant is a binary parameter that is equal to the slope of the sorption isotherm at infinite dilution. For this study, H was taken as an adjustable parameter since data were not available at the extremely low pressures necessary to determine an accurate infinite-dilution slope. The pure gas interaction energy, Γ_{gg}, was obtained from the equation-of-state form of this model (i.e., the Sanchez–Lacombe equation of state). An equivalent approach for determining the segment–segment interaction energy, Γ_{rr}, cannot be used for the glassy polymer since an equation of state is inappropriate (no unique volume for a given pressure and temperature). Two alternate approaches were used: (1) Γ_{rr} was taken as an adjustable parameter for both the CO_2–polycarbonate (PC) and CH_4–PC systems, and (2) Γ_{rr} was taken as adjustable for the CH_4–PC system and then this value was used for the CO_2–PC system. The gas–segment interaction parameter, Γ_{rg}, was set equal to the geometric mean of Γ_{gg} and Γ_{rr}.

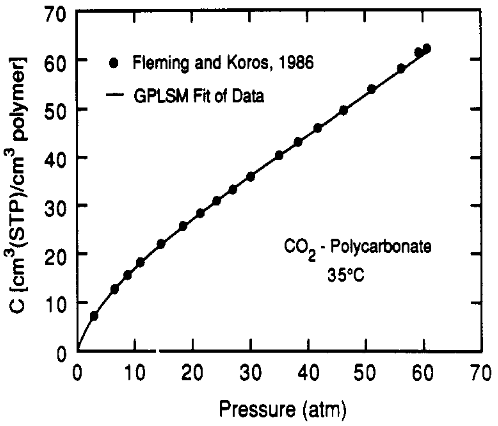

Figure 2. Carbon dioxide sorption in polycarbonate at 35 °C. The line represents the best fit of data using the glassy polymer lattice sorption model (GPLSM) with Γ_{rr} and H as adjustable parameters.

Finally, gas sorption data in glassy polymer systems are generally presented in the form of C (cm³ (STP)/cm³ of polymer) vs pressure. Data in this form are converted to the form used in the model, N_g/N_r, by the following expression:

$$\frac{N_g}{N_r} = \frac{C\hat{V}_s\hat{V}_T}{22415\hat{V}_{cp}} \tag{32}$$

where C is the concentration of the gas in the polymer in the units described above, $\hat{V}_s$ is the *molar* volume of a lattice site, and the factor 22415 converts cm³ (STP) to moles.

Results

Sorption isotherms for CO_2 and CH_4 in polycarbonate (PC) at 35 °C were fit by using GPLSM with H and Γ_{rr} as adjustable parameters. Data for these systems were obtained from Koros and co-workers.[10,16] The results are presented in Figures 2 and 3, and the resulting interaction energy parameters and Henry's law constants for these systems are presented in Table I.

The interaction energies, Γ_{ij}, in GPLSM have been written in Table I in terms of the more familiar ϵ/k, which is given by the expression

$$\epsilon_{ij}/k = -\Gamma_{ij}/k \tag{33}$$

where ϵ/k represents the mean depth of the potential energy well.

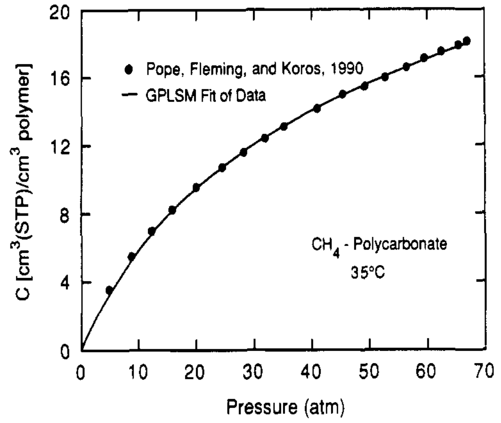

Figure 3. Methane sorption in polycarbonate at 35 °C. The line represents the best fit of data using the glassy polymer lattice sorption model (GPLSM) with Γ_{rr} and H as adjustable parameters.

The pure gas interaction energy parameters, ϵ_{gg}/k, were obtained from values of T^* from Sanchez and Lacombe (SL).[8] The SL T^* is defined as ϵ^*/k, where ϵ^*, the interaction energy per mer, is defined as $z\epsilon/2$. The size of a lattice site in GPLSM is taken to be the SL value of rv^*, the close-packed molecular volume for the penetrant gas molecule.[8] The molar lattice site volumes, $\hat{V}_s$, used in this study are 29.1 and 32.0 cm^3/mol for CO_2 and CH_4, respectively.[8,17] The ϵ_{gg}/k parameters in Table I were obtained by using a z of 10 for both systems and multiplying the SL ϵ/k per mer by the number of mers per gas molecule (4.36 and 6.6 for CH_4 and CO_2, respectively[8,17]).

The segment–segment energy parameter and the Henry's law constant were obtained by fitting binary gas–glassy polymer data with Γ_{rg} set equal to the geometric mean. The parameters for both systems were obtained by allowing both parameters to freely regress using a standard nonlinear least-squares regression routine. Since ϵ_{rr}/k represents a property of the pure polymer, the two values in Table I should only differ by the ratio of the hard-core volumes of the two penetrants since the lattice site volumes are different. Therefore, the ratio of ϵ_{rr}/k for the CO_2 system to ϵ_{rr}/k for the CH_4 system should be 0.91. The ratio from the regression analysis with two parameters is 0.88.

Using the ratio of 0.91, the value of ϵ_{rr}/k for the CO_2–PC system was set equal to 230.3 and only the Henry's law constant was allowed to freely regress. This *single-parameter* regression for CO_2–PC resulted in a value of 304.5 K for ϵ_{rg}/k (calculated from the geometric mean) and 207.9 atm for H. The resulting fit of the CO_2–PC sorption isotherm is shown in Figure 4. With only a single adjustable parameter, H, GPLSM gives an excellent fit of the data. The residual standard deviations for the two-parameter and single-parameter regressions for CO_2–PC are 0.25 and 0.49, respectively. The residual standard deviation for the dual-mode model for CO_2–PC is 0.23.[5]

Since the Henry's law constant represents the infinite-dilution (or initial) slope of the sorption isotherm, it could have been set to the experimental value of the initial slope instead of being regressed from binary data. However, accurate data were not available at the very low pressures necessary to obtain the infinite-dilution slope from the data.

The fraction of sites in the pure gas actually occupied by gas molecules, N_g'/N_T' is calculated from eq 25 to be 0.63 and 0.61 for CO_2 and CH_4, respectively, using $\hat{V}'$ values for CO_2 and CH_4 of 46.0[10] and 52.0 cm^3/mol,[18] respectively.

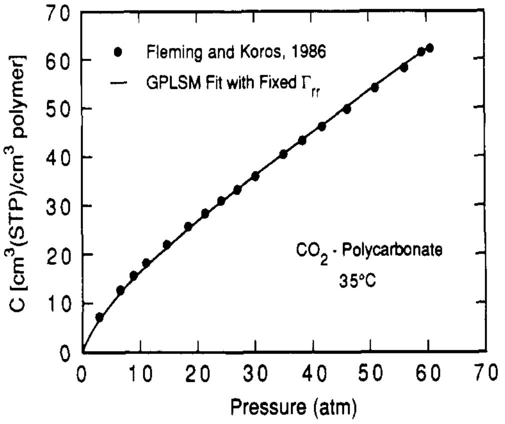

Figure 4. Carbon dioxide sorption in polycarbonate at 35 °C. The line represents the best fit of data using the glassy polymer lattice sorption model (GPLSM) with H as the only adjustable parameter.

Table I
GPLSM Parameters for the Polycarbonate (PC)–CO_2 and –CH_4 Systems at 35 °C Allowing ϵ_{rr}/k and H to Freely Regress for Both Systems ($\epsilon_{ij}/k = -\Gamma_{ij}/k$)

system	ϵ_{gg}/k,[a] K	ϵ_{rg}/k,[b] K	ϵ_{rr}/k, K	H, atm
PC–CO_2	402.6	299.1	222.2	185.0
PC–CH_4	190.8	219.7	253.3	702.0

[a] Obtained from Sanchez and Lacombe.[8] [b] Obtained from $\epsilon_{rg}/k = [(\epsilon_{gg}/k)(\epsilon_{rr}/k)]^{1/2}$.

Table II
***PVT* Properties for Polycarbonate at 1 atm[a]**

α_g	2.15×10^{-4} cm^3/(g K)	T_g	424.15 K
α_l	4.90×10^{-4} cm^3/(g K)	$\hat{V}_{T_g}$	0.864 cm^3/g

[a] Reference 19.

Table III
Parameters for Interpolative Correlation of Dilation Data (Eq 34; Pressure in atm)

system	α_0	β_0	γ_0
PC–CO_2	2.808×10^{-3}	1.200×10^{-3}	0.2673
PC–CH_4	5.755×10^{-3}	1.386×10^{-4}	0.0453

The initial number of holes in the polymer is determined from eqs 26 and 27 using the parameters in Table II. For polycarbonate, the initial hole fraction (N_h^0/N_r) is 0.28 at 35 °C. The manner in which the number of holes changes as a function of pressure is determined by eqs 30 and 31 using sorptive dilation data from the literature[10,16] for PC–CO_2 and PC–CH_4. Equations 30 and 31 indicate the need to know the derivative of the dilation isotherm at each point in the calculation. Since GPLSM must be solved numerically as a differential equation, dilation data are needed at an interval much smaller than is available in the literature. This necessitates a nonlinear interpolation. A correlation that fits the form of the dilation data is

$$\Delta V/V_0 = \beta_0 P + \alpha_0(1 - e^{-\gamma_0 P}) \qquad (34)$$

where P is pressure and α_0, β_0, and γ_0 are coefficients obtained by nonlinear least-squares regression of the experimental dilation data. This form of equation produces an excellent fit of the experimental dilation data, but other correlative fits of the dilation data, including polynomials, could also be used. The correlation parameters for the dilation data used in this paper are presented in Table III. It is important to remember that these are not adjustable parameters in GPLSM. Equation 34 is only used to aid in data interpolation and, in particular, the interpolation of the derivative of the data.

As mentioned above, GPLSM was solved numerically by using a standard fourth-order Runge–Kutta algorithm. The form of the equation solved is presented in the Appendix.

Discussion

The foregoing results indicate that an excellent fit of the experimental gas sorption data in glassy polymers is possible using GPLSM with reasonable values of the interaction energy parameters. Two adjustable parameters (Γ_{rr} and H) can be used to fit either the CH_4–PC or CO_2–PC data. If Γ_{rr} from the CH_4–PC system is used for the CO_2–PC system, then only one parameter (H) is necessary to give a reasonable fit of the data.

The major differences between GPLSM and other existing lattice-based models lie in the entropy of mixing term, the manner in which the number of holes on the lattice is specified, and how the number of holes changes as a function of pressure. The entropy term in GPLSM is unique in that it assumes that the polymer segments are immobile in the glassy polymer. This assumption begins to break down as the gas–glassy polymer mixture approaches its glass transition temperature, but it seems reasonable as a first approximation. At a pressure of 60 atm for CO_2–PC, it has been shown that the glass transition is lowered to 55 °C,[20] which is still above the measurement temperature of 35 °C.

The assumption of the presence of holes on the lattice is not a new one. It is a widely used assumption in many equations of state for equilibrium materials[7,8] and has also been used in models in the glassy region as a molecular ordering parameter.[6] In the work of Wissinger and Paulaitis,[6] the Panayiotou and Vera equation of state was fit in the equilibrium rubbery region and extrapolated into the glassy region with the value of the holes in the glassy region fixed to that calculated at the glass transition. This enabled Wissinger and Paulaitis to predict reasonably well the sorption behavior in the glassy region, but at temperatures well below the glass transition, where the curvature of the isotherms becomes significant, the fit was progressively worse. Our approach to holes below the glass transition is unique in that it uses a nonconstant value for the number of holes which changes as a function of gas pressure or concentration. Determination of the functional form of the change in the number of holes during gas sorption relies on having actual sorptive dilation data. The need for dilation data in GPLSM is a limitation of the model, but it also emphasizes the strong relationship between dilation and sorption.

GPLSM does not assume that there is a single population or two populations of sorbed gas. If a single population of gas were present, then each gas molecule would be expected to contribute equally to swelling by introducing the same amount of volume with each molecule. In other words, the partial molar volume of the penetrant would remain constant with increasing concentration. While this holds true for rubbery polymers, it has been shown not to be the case for glassy polymers.[10]

If two distinct populations are present and that population associated with the microvoids does not contribute to swelling, then linear swelling behavior should be observed with each gas molecule entering the "equilibrium" mode introducing the same amount of volume to the system. This approximation gives a very good physical representation of experimental observation for the PC–CO_2 system,[10] but the swelling isotherm, upon close examination does reveal nonlinearity. In addition, other systems show appreciable curvature in the swelling isotherm.[11-13,16]

GPLSM relies on the actual swelling data for information on how the gas molecules affect the volume. In the context of the dual-mode model, one may envision a size distribution of microvoids in the glassy polymer that will result in a distribution of partial molar volumes for the penetrant, ranging from 0 for gas molecules in nonswelling microvoids to a value associated with maximum swelling. This distribution is responsible for the nonlinearity observed in the dilation data. In more general terms, the free-volume distribution discussed above in the context of the dual-mode model can be extended to the entire polymer if the distribution of partial molar volumes encompasses the value for the equilibrium liquid. In these terms, GPLSM becomes, in effect, a multimode sorption model.

GPLSM can be used with polymer samples of different thermal history since the number of holes in the pure polymer can be used as a molecular ordering parameter to specify the particular nonequilibrium state of the glassy polymer sample.[6] GPLSM includes a term describing the nonideal volume change on mixing gas molecules with polymer. Although this term has been included for the sake of completeness, it has only a very minor effect on the results and can be completely omitted when using GPLSM. This term has been omitted in the expression for the activity coefficient in the Appendix.

Conclusion

The glassy polymer lattice sorption model (GPLSM) is a lattice-based activity coefficient model developed specifically for the case of gas sorption in glassy polymers. It recognizes the presence of holes on the lattice and requires thermal expansion data to calculate the number of holes initially on the lattice and sorptive dilation data to relate changes in the number of these holes to changes in polymer segment–segment interactions. Thus, it provides the essential link between polymer swelling due to penetrant gas molecules and gas sorption in glassy polymers. It produces an excellent fit of the experimental data with reasonable parameter values. Future work will center upon examining other gas–polymer systems including gas desorption hysteresis, extending the model to multicomponent gas mixtures, and relaxing the assumption of polymer immobility involved in the entropy term.

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Appendix

The following equation is the GPLSM expression for the natural logarithm of the activity of the gas in the glassy polymer:

$$\ln a_g = \left(\frac{\partial \frac{\Delta G_{mix}}{kT}}{\partial N_g}\right)_{P_T,T,N_r} = \left(\frac{\partial \frac{\Delta U_{mix}}{kT}}{\partial N_g}\right)_{P_T,T,N_r} + \left(\frac{\partial \frac{P\Delta V_{mix}}{kT}}{\partial N_g}\right)_{P_T,T,N_r} - \left(\frac{\partial \frac{\Delta S_{mix}}{k}}{\partial N_g}\right)_{P_T,T,N_r} \quad (35)$$

where

$$\left(\frac{\partial\frac{\Delta U_{\text{mix}}}{kT}}{\partial N_g}\right)_{P_T,T,N_r} = \frac{z}{kT}\Bigg[-\frac{N_rN_{r,nc}}{N_T^{\,2}}\left(1+\frac{\partial N_h}{\partial N_g}\right)\frac{\Gamma_{rr}}{2} + \frac{N_r}{N_T}\Gamma_{rg} - \frac{N_gN_r}{N_T^{\,2}}\left(1+\frac{\partial N_h}{\partial N_g}\right)\Gamma_{rg} + 2\frac{N_g}{N_T}\frac{\Gamma_{gg}}{2} - \left(\frac{N_g}{N_T}\right)^2\left(1+\frac{\partial N_h}{\partial N_g}\right)\frac{\Gamma_{gg}}{2} - \frac{z_g}{z}\frac{\Gamma_{gg}}{2}\Bigg] \quad (36)$$

and

$$z_g = z(N_g'/N_T') \quad (37)$$

and

$$\left(\frac{\partial\frac{P\Delta V_{\text{mix}}}{kT}}{\partial N_g}\right)_{P_T,T,N_r} = \frac{PV_s}{kT}\left(\frac{\partial N_h}{\partial N_g} - \frac{1-z_g}{z_g}\right) \quad (38)$$

and

$$-\left(\frac{\partial\frac{\Delta S_{\text{mix}}}{k}}{\partial N_g}\right)_{P_T,T,N_r} = \ln\frac{N_g}{N_g+N_h} + \frac{\partial N_h}{\partial N_g}\ln\frac{N_h}{N_g+N_h} - \ln\frac{z_g}{z} \quad (39)$$

Subtraction of the natural logarithm of N_g/N_r from the natural logarithm of the activity produces the following expression for the activity coefficient of the gas in the glassy polymer:

$$\ln\gamma_g = \ln a_g - \ln(N_g/N_r) \quad (40)$$

Upon substitution of eqs 30 and 31 for $1 + \partial N_h/\partial N_g$ into the activity coefficient expression, it is apparent that the equation cannot be solved analytically. Thus, the expression is rearranged into the following form to facilitate a numerical solution:

$$\frac{\partial P}{\partial\frac{N_g}{N_r}} = \frac{\frac{\partial\Delta\hat{V}}{\partial\frac{N_g}{N_r}}}{\frac{\partial\Delta\hat{V}}{\partial P}} = \frac{\left(1+\frac{\partial N_h}{\partial N_g}\right)\hat{V}_{cp}}{\frac{\partial\Delta\hat{V}}{\partial P}} \quad (41)$$

where

$$1+\frac{\partial N_h}{\partial N_g} = \left\{\ln\gamma^* + \ln\frac{N_h}{N_r} + \ln z_g - \frac{z}{kT}\left(\frac{N_r}{N_T}\Gamma_{rg} + \frac{N_g}{N_T}\Gamma_{gg} - \frac{z_g}{z}\frac{\Gamma_{gg}}{2}\right) + \ln\gamma^\infty\right\}\Bigg/\left\{\ln\frac{N_h}{N_g+N_h} - \frac{z}{kT}\left(\frac{N_rN_{r,nc}}{N_T^{\,2}}\frac{\Gamma_{rr}}{2} + \frac{N_gN_r}{N_T^{\,2}}\Gamma_{rg} + \left(\frac{N_g}{N_T}\right)^2\frac{\Gamma_{gg}}{2}\right)\right\} \quad (42)$$

γ^* is the *asymmetrically* normalized activity coefficient given by the equilibria expression

$$\gamma^* = \frac{f_g}{\frac{N_g}{N_r}H} \quad (43)$$

and $\ln\gamma^\infty$, the natural logarithm of the infinite-dilution activity coefficient, is given by

$$\ln\gamma^\infty = -\ln\frac{N_h^{\,0}}{N_r} - \ln z_g + \frac{z}{kT}\left[-\left(\frac{N_r}{N_T^{\,0}}\right)^2 f\frac{\Gamma_{rr}}{2}\left(1+\frac{\partial N_h}{\partial N_g}\right)_0 + \frac{N_r}{N_T^{\,0}}\Gamma_{rg} - \frac{z_g}{z}\frac{\Gamma_{gg}}{2}\right] \quad (44)$$

where the derivative of the number of holes at infinite dilution with respect to the number of gas molecules is determined by taking the limit of eqs 30 and 31 at zero gas conditions. It is given by the following expression:

$$\left(1+\frac{\partial N_h}{\partial N_g}\right)_0 = \frac{H}{\hat{V}_{cp}}\left(\frac{\partial\Delta\hat{V}}{\partial P}\right)_0 \quad (45)$$

where $(\partial\Delta\hat{V}/\partial P)_0$ is determined from the infinite-dilution slope of the experimental sorptive dilation data.

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