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A Thermodynamic Analysis of Gas Sorption–Desorption Hysteresis in Glassy Polymers

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ABSTRACT: Sorption–desorption isotherms for carbon dioxide in polycarbonate, tetramethylpolycarbonate, hexafluoropolycarbonate, and poly(vinyl benzoate) were fitted using the glassy polymer lattice sorption model (GPLSM). The model requires sorptive dilation data to account properly for lattice compressibility. Using polymer segment–segment interaction energies from the sorption isotherms, the desorption isotherms were fitted with only a single adjustable parameter, the Henry's law constant. Differences in Henry's law constants between sorption and desorption were explained in terms of the unoccupied volume before and after the sorption–desorption process and the "volatility" of the gas in the local polymer environment at infinite dilution.

Introduction

A quantitative description of the thermodynamics of gas sorption in glassy polymers is important in membrane-based gas separations, barrier applications, and polymer impregnation processes. Gas sorption and desorption isotherms in glassy polymers exhibit hysteretic behavior,[1,2] a manifestation of the long relaxation times associated with this nonequilibrium state. This is in contrast to the behavior in rubbery polymers in which the sorption and desorption isotherms coincide. In glassy polymers that are plasticized at high pressures, hysteresis is observed below the pressure corresponding to the glass transition concentration, but the isotherms coincide above this pressure.

A number of models have been used to quantify gas sorption in glassy polymers. The most widely used of these is the dual mode sorption model.[3–5] The dual mode model assumes that two distinct populations of gas molecules exist within the glassy polymer, one in which molecules are sorbed by an ordinary dissolution mechanism and one in which molecules reside in the preexisting gaps frozen into the glassy polymer as it was cooled through the glass transition temperature. Local equilibrium is assumed to exist between the two populations of penetrant molecules. The parameters of this model have been given physical interpretations which are used successfully to explain much of the observed behavior associated with gas sorption in glassy polymers.

Although the dual-mode model can be used to fit a gas desorption isotherm in a glassy polymer, the resulting parameters cannot be given physical significance relative to those parameters for the corresponding sorption isotherm.[2] Recently, an activity coefficient model based on a compressible lattice was developed for gas sorption in glassy polymers. The model, the glassy polymer lattice sorption model (GPLSM), is used here to analyze gas sorption–desorption hysteresis. Only two adjustable parameters are required for a given gas–polymer pair, a segment–segment interaction energy, and a Henry's law constant that reflects the initial slope of the isotherm.

In a previous study,[6] we used this model to demonstrate that gas sorption isotherms before and after exposure to high gas pressure could be analyzed with a single segment–segment interaction energy. The terms, unconditioned and conditioned, are used to refer to the polymer before and after exposure, respectively. Only one adjustable parameter, the Henry's law constant, was necessary for the conditioned isotherm. Similarly, in this paper, the segment–segment interaction energy from a sorption isotherm will be fixed for the desorption isotherm with the Henry's law constant as the only adjustable parameter.

Background

Classic Flory–Huggins theory was developed for an incompressible lattice on which there is no volume change of mixing. This is a reasonable assumption for gas–rubbery polymer mixtures but has been shown to be inadequate for gas–glassy polymer systems.[6] The glassy polymer lattice sorption model (GPLSM) was developed specifically to account for lattice compressibility for these systems. The expression for ΔG_{mix} from GPLSM is very similar to that resulting from Flory–Huggins theory, but the application to gas sorption data in glassy polymers requires sorptive dilation or swelling data for the gas–polymer mixture to account for the compressibility of the lattice.

For a compressible lattice containing gas molecules (N_g), polymer segments (N_r), and holes (N_h), ΔG_{mix} is given by[7]

$$\frac{\Delta G_{\text{mix}}}{kT} = N_g \ln \frac{N_g}{N_g + N_h} + N_h \ln \frac{N_h}{N_g + N_h} - N_g' \ln \frac{N_g'}{N_g' + N_h'} - N_h' \ln \frac{N_h'}{N_g' + N_h'} + \Psi \frac{N_g N_r}{N_g + N_r + N_h} + \frac{PV_s}{kT}(N_T - N_T^0 - N_T') \quad (1)$$

where

$$\Psi = \frac{z}{kT}\left[\Gamma_{rg} - \frac{1}{2}(\alpha\Gamma_{gg} + \beta\Gamma_{rr})\right] \quad (2)$$

$$\alpha = \frac{N_g'}{N_T'}\left(\frac{N_T - N_T'}{N_r}\right) \quad (3)$$

and

$$\beta = \frac{F N_r}{N_T^0}\left(\frac{N_T - N_T^0}{N_g}\right) \quad (4)$$

Physically, α and β account for the compressibility of the lattice. F is the fraction of polymer segments that interact

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noncovalently. For high molecular weight polymers, F is given by

$$F = \frac{z-2}{z} \tag{5}$$

where z is the coordination number. N_T is the total number of lattice sites in the mixture ($N_g + N_r + N_h$), N_T^0 is the number of sites in the pure polymer ($N_r + N_h^0$), and N_T' is the number of sites in the pure gas. N_g'/N_T' is the fraction of sites in the pure gas occupied by gas molecules, and V_s is the molecular lattice-site volume which, in the present work, is equal to the close-packed molecular volume of the gas.

The first two terms in eq 1 represent the combinatorial entropy associated with placing gas molecules on a lattice containing polymer segments and holes. The assumption here is that the polymer segments do not contribute to the combinatorial entropy of mixing for the glassy system. This is similar to the assumption made by others to describe the entropy of a polymer at temperatures below the glass transition[8,9] and is a reasonable first approximation provided the mixture remains glassy. The second two terms represent the entropy of the pure gas which also contains holes on its lattice. The fifth term is the internal energy contribution which is very similar to the enthalpic contribution in Flory–Huggins theory based on a mean-field approximation. The sixth and final term in eq 1 is the volume of mixing term which is not zero for a compressible lattice. However, this term is small in magnitude compared to the others and is not included in further analysis.[7] The compressibility of the lattice is reflected in the term for the internal energy.

Equation 1 can be developed into an activity coefficient model using the equations

$$kT \ln a_g = \left(\frac{\partial\, \Delta G_{mix}}{\partial N_g}\right)_{P,T,N_r} \tag{6}$$

$$a_g = \gamma_g \frac{N_g}{N_r} \tag{7}$$

$$\gamma_g^* = \gamma_g / \gamma_g^\infty \tag{8}$$

and

$$f_g = \gamma_g^* \frac{N_g}{N_r} H \tag{9}$$

where a_g is the activity of the gas in the polymer, γ_g and γ_g^* are the symmetrically- and asymmetrically-normalized activity coefficients for the gas in the polymer, respectively, f_g is the gas-phase fugacity, γ_g^∞ is the symmetrically normalized activity coefficient at infinite dilution, and H is Henry's law constant.

The application of eq 6 to eq 1 results in a complex activity coefficient expression owing to the derivative, $\partial N_h/\partial N_g$. If the lattice were incompressible, but contained holes, this derivative would be zero and a simple analytical expression would result. Rearranging the expression for $\ln \gamma^*$ that results from applying eqs 6–9 and solving for $\partial N_h/\partial N_g$ gives

$$1 + \frac{\partial N_h}{\partial N_g} = \left[\ln \gamma^* + \ln \frac{N_h}{N_r} + \ln z_g - \frac{z}{kT}\left(\frac{N_r}{N_T}\Gamma_{rg} + \frac{N_g}{N_T}\Gamma_{gg} - \frac{z_g}{z}\frac{\Gamma_{gg}}{2}\right) + \ln \gamma^\infty\right] \Big/ \left[\ln \frac{N_h}{N_g + N_h} - \frac{z}{kT}\left(F\left(\frac{N_r}{N_T}\right)^2 \frac{\Gamma_{rr}}{2} + \frac{N_g N_r}{N_T^2}\Gamma_{rg} + \left(\frac{N_g}{N_T}\right)^2 \frac{\Gamma_{gg}}{2}\right)\right] \tag{10}$$

where

$$z_g = z\left(\frac{N_g'}{N_T'}\right) \tag{11}$$

and

$$\ln \gamma^\infty = -\ln \frac{N_h^0}{N_r} - \ln z_g + \frac{z}{kT}\left[-F\left(\frac{N_r}{N_T^0}\right)\frac{\Gamma_{rr}}{2} \times \left(\frac{d\left(\frac{\Delta V}{V_0}\right)}{dp}\right)_0 H + \frac{N_r}{N_T^0}\Gamma_{rg} - \frac{z_g}{z}\frac{\Gamma_{gg}}{2}\right] \tag{12}$$

The "0" subscript on the derivative of $\Delta V/V_0$ with respect to pressure refers to the initial slope of the dilation isotherm. The number of holes depends on both dilation and sorption through the expression

$$\frac{N_h}{N_r} = \frac{N_h^0}{N_r} + \frac{\hat{V}_{sp}}{\hat{V}_{oc}}\left(\frac{\Delta V}{V_0}\right) - \frac{N_g}{N_r} \tag{13}$$

where $\hat{V}_{sp}$ is the specific volume of the polymer and $\hat{V}_{oc}$ is the occupied volume as determined from Bondi's group contribution method.[10] $\hat{V}_{sp} - \hat{V}_{oc}$ is the total free volume in the pure polymer which is related to the initial number of holes, N_h^0. Since $\hat{V}_{sp}$ is dependent on history for a glassy polymer, N_h^0 is, in a sense, an ordering parameter describing a particular glassy state. However, regardless of the thermal or gas conditioning history of the sample, N_r remains constant for a compressible lattice. The ratio $\hat{V}_{sp}/\hat{V}_{oc}$ is equal to the ratio N_T^0/N_r and the ratio $(\hat{V}_{sp} - \hat{V}_{oc})/\hat{V}_{oc}$ is equal to the ratio N_h^0/N_r.

The derivative $\partial N_h/\partial N_g$ can also be written as

$$1 + \frac{\partial N_h}{\partial N_g} = \frac{d\left(\frac{\Delta V}{V_0}\right)}{d\left(\frac{N_g}{N_T^0}\right)} = \frac{d\left(\frac{\Delta V}{V_0}\right)}{dp}\,\frac{dp}{d\left(\frac{N_g}{N_r}\right)}\,\frac{N_T^0}{N_r} \tag{14}$$

Equations 10 and 14 can be solved for γ_g^* which, with eq 9, gives a differential equation for the final expression describing the gas sorption isotherm in a glassy polymer. The numerical procedure used to solve this equation is based on a Runge–Kutta algorithm and is given elsewhere.[7] Using an appropriate value of Γ_{gg}/k and the geometric mean for Γ_{rg}/k, GPLSM has two adjustable parameters, Γ_{rr}/k and H.

Previously, we demonstrated the application of GPLSM to sorption isotherms for a number of gas–polymer systems.[6] In the present study, we examine available sorption–desorption data for a single gas, carbon dioxide, in four glassy polymers. In the development of GPLSM,[7] Γ_{rr}/k represents a polymer segment–segment interaction energy. On a compressible lattice with holes and in the context of eq 1 for ΔG_{mix}, Γ_{rr}/k can be related to the cohesive energy density (CED) of the polymer by

$$\mathrm{CED} = \frac{-zF}{2}\frac{\Gamma_{rr}}{k}\frac{R}{\bar{V}_s}\frac{\hat{V}_{oc}}{\hat{V}_{sp}} \tag{15}$$

where $\bar{V}_s$ is the molar volume of a lattice site (29.13 cm^3/mole based on CO_2) and R is the gas constant. From this expression, it is obvious that the CED is dependent on sample history through $\hat{V}_{sp}$. However, Γ_{rr}/k is independent of sample history and should be the same for both sorption and desorption. In earlier work, we have shown that once

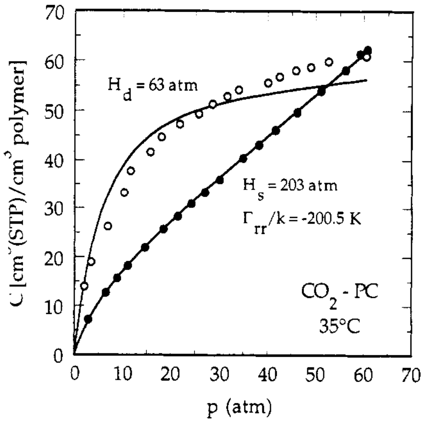

Figure 1. Sorption (closed circles)–desorption (open circles) hysteresis for carbon dioxide in unconditioned polycarbonate (PC) at 35 °C (data from ref 2). Curves represent best fits using the glassy polymer lattice sorption model with Γ_{rr}/k and H_s as adjustable parameters for the sorption isotherm and H_d as the single parameter for the desorption isotherm.

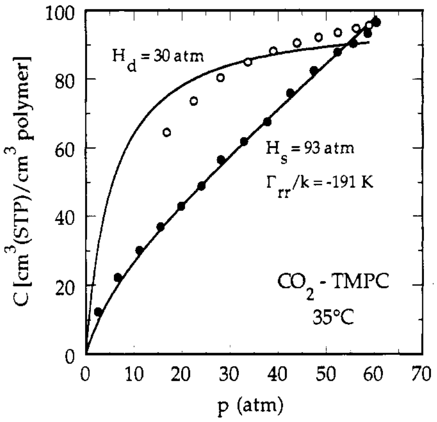

Figure 2. Sorption (closed circles)–desorption (open circles) hysteresis for carbon dioxide in unconditioned tetramethylpolycarbonate (TMPC) at 35 °C (data from ref 2). Curves represent best fits using the glassy polymer lattice sorption model with Γ_{rr}/k and H_s as adjustable parameters for the sorption isotherm and H_d as the single parameter for the desorption isotherm.

Γ_{rr}/k is determined for a single gas–polymer pair, this value can then be fixed for conditioning effects or for other gases in the same polymer.[6] Here, we will determine Γ_{rr}/k from a sorption isotherm and use this value to model the desorption isotherm.

Since the close-packed molecular volume of carbon dioxide from the Sanchez–Lacbome equation of state is used to define the lattice-site volume, the value of Γ_{gg}/k for CO_2 was taken from a fit of pure gas data with the Sanchez–Lacombe equation of state. The value of Γ_{gg}/k for CO_2 used here is −402.6 K.[11] Gas concentration in the typical units of $cm^3(STP)/cm^3$ of polymer is converted to N_g/N_r for GPLSM using the equation

$$\frac{N_g}{N_r} = \frac{C\,\bar{V}_s}{22415}\,\frac{\hat{V}_{sp}}{\bar{V}_{oc}} \qquad (16)$$

where the factor, 22415, converts $cm^3(STP)$ to moles.

Results and Discussion

Sorption and desorption isotherms for CO_2 in polycarbonate, tetramethylpolycarbonate, and hexafluoropolycarbonate at 35 °C and for CO_2 in poly(vinyl benzoate) at 25 °C are shown in Figures 1–4, respectively. The solid circles represent the sorption (or pressure increasing) data and the open circles represent the desorption (or pressure decreasing) data. Sorption and dilation data for the three

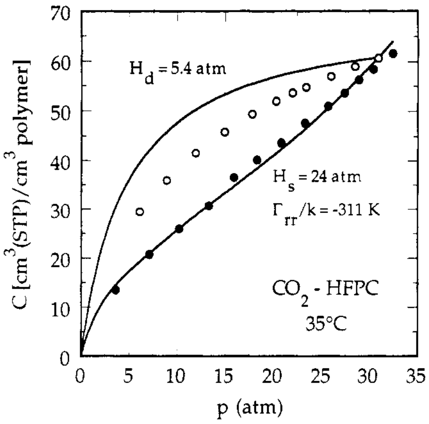

Figure 3. Sorption (closed circles)–desorption (open circles) hysteresis for carbon dioxide in unconditioned hexafluoropolycarbonate (HFPC) at 35 °C (data from ref 2). Curves represent best fits using the glassy polymer lattice sorption model with Γ_{rr}/k and H_s as adjustable parameters for the sorption isotherm and H_d as the single parameter for the desorption isotherm.

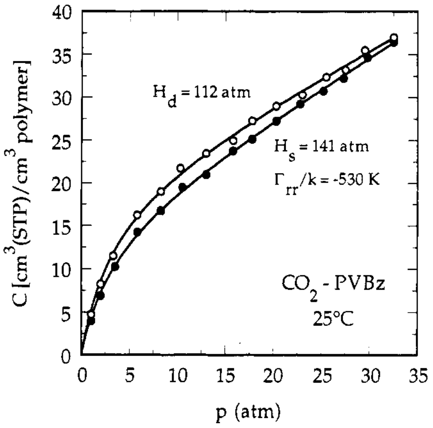

Figure 4. Sorption (closed circles)–desorption (open circles) hysteresis for carbon dioxide in conditioned poly(vinyl benzoate) at 25 °C (data from ref 12). Curves represent best fits using the glassy polymer lattice sorption model with Γ_{rr}/k and H_s as adjustable parameters for the sorption isotherm and H_d as the single parameter for the desorption isotherm.

polycarbonates were taken from Fleming.[2] The data for poly(vinyl benzoate) was extracted from a paper by Kamiya et al.[12] For the three polycarbonates, the sorption isotherms are for unconditioned samples. The sorption isotherm for the poly(vinyl benzoate) is for a conditioned sample.

The sorption isotherms in Figures 1–4 were fitted with GPLSM using two adjustable parameters, Γ_{rr}/k and H_s, where "s" denotes sorption. The values of the parameters are listed on the figures. The swelling isotherm, $\Delta V/V_0$ versus pressure, was used to determine how the number of holes in the system changes. The curves through the desorption data are the GPLSM fits using one adjustable parameter, H_d, where "d" denotes desorption. Henry's law coefficients are lower for desorption than for sorption. Since $1/H$ represents the slope of the isotherm at infinite dilution when plotted as N_g/N_r versus fugacity, H_d should be less than H_s. More satisfying, however, are the reasonable single-parameter fits of the desorption isotherms.

Fleming[2] attempted to interpret sorption–desorption hysteresis in terms of the dual mode model for gas sorption in glassy polymers. The relationship between concen-

Table I. GPLSM Henry's Law Constants and Polymer Hole Fractions at Zero Pressure for Unconditioned Sorption, Conditioned Sorption, and Desorption

polymer	history	H, atm	hole fraction
PC	1st sorption	203	0.163
PC	desorption	63	0.169
PC[a]	2nd sorption	118	0.169
TMPC	1st sorption	93	0.179
TMPC	desorption	30	0.201
TMPC[a]	2nd sorption	60.4	0.201
HFPC	1st sorption	24	0.195
HFPC	desorption	5.4	0.200
PVBz	2nd sorption	141	0.171
PVBz	desorption	112	0.173

[a] From ref 6.

tration, C, and pressure, p, for this model is

$$C = k_{\rm D}p + \frac{C_{\rm H}'\,bp}{1 + bp} \tag{17}$$

where $k_{\rm D}$ is the solubility coefficient for the gas population sorbed by ordinary dissolution, $C_{\rm H}'$ is the saturation concentration for molecules sorbed into unrelaxed sites in the glassy polymer, and b is the affinity constant for these sites. In general, Fleming found a large decrease in $k_{\rm D}$ and a large increase in $C_{\rm H}'$ for desorption compared to sorption. However, from the dilation and sorption data, the partial specific volumes were similar for both sorption and desorption. Therefore, he concluded that hysteresis cannot be rationalized from a dual mode analysis. Instead, he hypothesized that sorption causes a change in the cohesive energy density (CED) of the gas–polymer mixture which influences the desorption concentration at the same gas activity.

For gas solubility on an incompressible lattice without holes, Henry's law constant, as used here, is a measure of the "volatility" of the gas in the liquid or polymer at infinite dilution.[6] If it is difficult for the gas molecule to create a hole owing to strong intermolecular forces between liquid molecules, H will be higher in that particular solvent than in one in which the interactions are weak. Thus, Henry's law constant is higher in polar solvents than nonpolar ones. Similarly, in the case of preexisting holes in glassy polymers with different thermal histories, the greater the number of holes, the weaker the intermolecular forces averaged over the entire volume and, hence, the lower the Henry's law constant. If the gas molecules do not have to create holes, they will be less "volatile" in that particular environment.

Based on this interpretation of the Henry's law constant from GPLSM, the magnitude of H should be related to the number of holes initially in the polymer. This relationship is shown in Figure 5 for the sorption–desorption isotherms in Figures 1–4 and conditioned isotherms fit using GPLSM from a previous study.[6] The initial polymer hole fraction is equal to $(\hat{V}_{\rm sp} - \hat{V}_{\rm oc})/\hat{V}_{\rm sp}$. Table I lists the polymers and sorption histories that correspond to the points in Figure 5.

There is a general trend in Figure 5 indicating tht H, in part, is determined by the initial number of holes in the system. However, the initial hole fraction for a desorption isotherm is the same as for a second sorption isotherm, but the values of H are different. This is shown in Table I and Figure 5 for polycarbonate and tetramethylpolycarbonate. In addition to the number of holes, the distribution of gas molecules at infinite dilution must also influence the magnitude of H. Although the number of holes is the same and $\Gamma_{\pi\pi}/k$ is constant, the last gas molecules to leave the polymer during desorption may be distributed among the holes differently than those molecules that first entered during sorption.

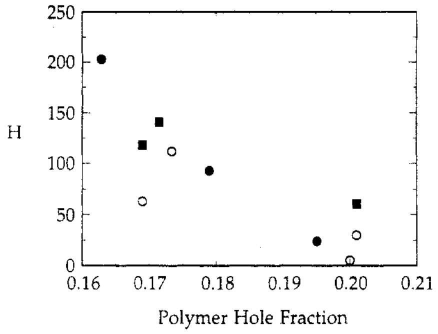

Figure 5. Relationship between Henry's law constant for CO_2 from GPLSM and the polymer hole fraction (unconditioned first sorption, solid circles; desorption, open circles; conditioned second sorption, solid squares).

Conclusions

Gas sorption–desorption hysteresis in glassy polymers can be interpreted thermodynamically with the glassy polymer lattice sorption model (GPLSM). Using the polymer segment–segment interaction energy from the sorption isotherm, the desorption isotherm can be modeled with a single adjustable parameter, Henry's law constant. The magnitude of Henry's law constant is influenced by the amount of unoccupied volume in the polymer and the local environment experienced by the gas molecules at infinite dilution.

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