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Direct Measurement of the Heat of Carbon Dioxide Sorption in Polymeric Materials

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ABSTRACT: Direct measurements of the partial molar enthalpy of carbon dioxide sorption in polycarbonate and poly(dimethylsiloxane) are reported. Sorption is a highly exothermic process. The heat of sorption in poly(dimethylsiloxane) is constant, ~−1.5 kcal/mol, up to 300 psig, and the value does not depend on whether the measurements are made during pressurization or depressurization. For polycarbonate, however, the magnitude of the enthalpy change is much greater, varying from −3.5 to −5 kcal/mol. This increase is attributed to the presence of excess free volume in the glassy polycarbonate, which makes sorption energetically comparable to vapor condensation. If measurements are made during depressurization immediately after pressurization, the partial molar enthalpy of sorption increases dramatically. We attribute this behavior to gas plasticization effects during pressurization since preconditioning the sample at the maximum exposure pressure eliminates the difference. The magnitude of the partial molar enthalpy of sorption increases if the sample is preconditioned at increasing carbon dioxide pressures. Furthermore, the value is constant over a broad pressure range, from 0 to ~300 psig. A constant value is not consistent with a multiple-site sorption mechanism unless the heat of sorption is the same for all sites or the relative occupancy of each site remains constant.

Introduction

Gas sorption in polymeric materials is critical to membrane separation[1] and barrier applications.[2] In the former, one desires a material with high gas solubilities and large solubility selectivity for gas mixtures, while the latter requires a material with low gas solubilities.

To characterize the solubility of a gas–polymer system, the most common measurements are mass uptake[3] and volume dilation.[4] The absolute solubility obtained from mass uptake measurements is the key material property required either to design a membrane separation system or to specify barrier requirements. Volume dilation measurements provide additional insight into the physics of gas sorption and the nature of gas–polymer interactions. In particular, gas partial molar volumes in the polymer are lower than in low molecular weight liquids. This is attributed to the presence of excess free volume in the glassy state, as discussed later.

Solubility measurements over a temperature range also give estimates of the apparent heat of gas sorption. One may use the van't Hoff or Clausius–Clapeyron equation to extract the heat of sorption from these measurements. How the apparent heat of sorption varies with concentration and with the specific gas–polymer system provides additional insight into gas–polymer interactions. For example, the temperature dependence of the solubility indicates that sorption in glassy polymers is much more exothermic than in rubbery polymers. The highly exothermic nature of sorption in glasses reflects the presence of excess free volume,[5] since penetrant molecules may occupy a portion of the glass excess free volume, sorption becomes energetically equivalent to vapor condensation.

Correlation or interpretation of gas sorption measurements commonly relies upon the dual mode model.[5,6] The dual mode model assumes that two different sorption environments or sites exist in glassy polymeric materials. The excess free volume of the glass provides one sorption environment. Since the available excess free volume is limited, these sorption sites are referred to as the Langmuir sorption mode and are described by a Langmuir sorption isotherm in analogy to adsorption on a fixed number of surface sites. The remaining dense polymer regions constitute a second sorption environment. This environment is the only one available in the rubbery state. Sorption in these regions is referred to as the Henry's law mode and is described by a Henry's law constant in analogy to absorption in liquids.

The literature contains numerous theoretical alternatives to the dual mode model.[7] These include models based on the principles of concentration–temperature superposition,[8] multiple Langmuir sorption modes,[9] modified lattice fluid theories,[10–14] sorption in elastic solids,[15] and molecular models.[16] All are capable of describing pure gas sorption isotherms, while certain models have demonstrated the ability to predict mixed gas sorption based on material properties obtained from pure gas sorption data[17,18] and others offer the potential to predict gas partial molar volume.[8]

Each of the proposed models uses physically realistic material parameters to represent mass uptake and volume dilation data. This makes discrimination between the alternatives difficult in the absence of additional experimental characterization of sorption. We report direct measurements of the heat of gas sorption that give a different perspective on the nature of gas–polymer interactions and will hopefully prove useful in the development of and discrimination between sorption models. Results are presented for two gas–polymer systems: carbon dioxide–polycarbonate (PC) and carbon dioxide–poly(dimethylsiloxane) (PDMS). These systems allow us to compare sorption in a polymeric glass and rubber.

An extensive material property database (CO_2 solubility, diffusivity, and partial molar volume) exists for

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Table 1. Comparison of Experimental and Literature Values[26] for the Fusion Temperatures and Heat of Fusion of Gallium and Indium

	T_f (°C)		ΔH_f (cal/g)	
substance	exp	lit.	exp	lit.
gallium	29.8	29.8	18.9	19.1
indium	157.5	156.9	6.7	6.8

the CO_2–PC and CO_2–PDMS systems at 35 °C. We will use the solubility measurements to extract heats of sorption from the calorimetric data. Heat of sorption measurements in PC over a temperature range that spans its glass transition would allow us to compare a glass and rubber of the same chemical composition. However, we performed experiments only at 35 °C since solubility data are not available over such a temperature range. Such measurements are certainly of interest once experimental solubility data are available.

Experimental Procedure

To measure the enthalpic changes that accompany sorption, we utilize a Setaram C80D microcalorimeter (Astra Scientific Inc.) equipped with the optional high-pressure flow cells. The instrument possesses a sensitivity of approximately 10 μW. One may operate the calorimeter in either a scanning or isothermal mode.

The calorimeter's temperature and heat flow calibrations were checked through scanning measurements of the fusion of gallium and indium (Aldrich) samples. These materials melt at temperatures that bracket the experimental temperature of 35 °C. Table 1 indicates the experimental fusion temperature and heat of fusion are in excellent agreement with literature values.

The high-pressure cells, a sample and reference, possess a volume of roughly 12 cm^3. External ports permit the introduction and removal of a high-pressure, up to 1000 psia, gas stream to both cells. In this work, the cell inlets were connected to a high-pressure gas cylinder while the outlets were closed; see Figure 1. This allows simultaneous pressurization of both cells.

Thin films of PC were used in the experiments. To prepare the films, as-received PC pellets (Aldrich) were dissolved in methylene chloride (Aldrich) to prepare a 10% by weight solution. This solution was cast on a glass plate using a casting knife (Gardner) and allowed to dry under ambient atmospheric conditions for 10–24 h. The films were placed under vacuum and allowed to dry at ambient temperature for an additional 24 h. Finally, each sample was annealed under vacuum at 130 °C for 3 days prior to an experimental run. Ultimate film thicknesses were approximately 15 μm.

Sheets of PDMS were provided by Professor J. Mark of the Chemistry Department at the University of Cincinnati. The samples possessed a cross-link density of 5.5×10^{-5} mol/cm^3 and were 420 μm thick.

The experimental procedure consists of

1. Place a known polymer mass and volume in the sample cell.
2. Evacuate both cells.
3. Expose the sample to a prescribed carbon dioxide (99.8%) pressure for 24 h at 35 °C. Rapidly change the pressure to the initial experimental pressure: conditioned PC samples only.
4. Set temperature to the experimental temperature of 35 °C.
5. Establish a baseline heat flow.
6. Either rapidly increase or decrease the pressure in both the sample and reference cells by approximately 50 psig.
7. Record enthalpic changes until a new baseline is established.
8. Repeat steps 6 and 7 until either the maximum or minimum desired pressure is reached.

Note that all experiments are isothermal. The experimental temperature, 35 °C, corresponds to a temperature for which the solubility of carbon dioxide in both polymers is well characterized.[4,19–22]

Ideally, the heat flow would reflect only the enthalpic changes in the gas–polymer system which accompany gas sorption in the polymer. However, two major sources of unwanted thermal artifacts are Joule–Thompson cooling of the gas and differences in pressure–volume work between the two cells due to differences in gas volume.

To address these issues, three modifications were made to the basic experimental setup described previously; see Figure 1. First, a high-pressure reservoir (300 cm^3) was placed between the gas cylinder and the cells. This allows one to reduce the gas pressure from that of the cylinder to that of the experiment prior to introducing the gas into the cells. Therefore the pressure differential that the gas experiences upon entering the cell is equal to the pressure increment, not the difference between the experimental and cylinder pressures. For depressurization experiments, one sets the reservoir pressure slightly below the next desired pressure so the gas expands from the cells to the desired pressure and not to atmospheric pressure. By reducing the magnitude of the pressure change associated with gas introduction or removal, Joule–Thompson thermal effects are minimized.

Second, a volume of glass beads equal to that of the sample is placed in the reference cell. This makes the gas volume of the sample and reference comparable and reduces differences in pressure–volume work during pressure changes.

Third, identical stainless steel sample holders were made for the sample and reference cells. The inserts consist of a mesh cylinder supported by three legs and capped by a solid lid. They hold the sample in the center of the measurement zone, promote good gas contact with the sample, and make gas flow patterns within the cells more uniform during pressure changes.

Data Analysis

Figure 2 illustrates typical experimental measurements. The raw data consist of heat flow measurements as a function of time. Figure 2 shows these measurements for a series of pressure increases. The heat flow rising rapidly from the baseline corresponds to a pressure increase. After passing through some maximum, the heat flow decreases back to the baseline.

To convert these measurements to heats of sorption, a linear baseline was established for each pressure increment by connecting the baselines before and after the pressure change; see Figure 2. The area between the heat flow curve and baseline was then determined using the analysis software provided with the calorimeter.

This area is equal to the heat change that accompanies the transfer of n_i moles of carbon dioxide from the gas phase at the given experimental temperature, $T = 35$ °C, and pressure, p_i, to the polymer after the imposed pressure change from p_{i-1} to p_i; the subscript i denotes the value associated with ith pressure change from the initial experimental pressure, p_0. The total gas concentration in the polymer after the ith pressure change, N_i, is given by

$$N_i = \sum_{j=1}^{i} n_j \qquad (1)$$

For the glassy PC, we will use the dual mode model to relate N_i to p_i,

$$\frac{22400 N_i}{V} = c(f_i) = k_d f_i + \frac{b C'_H f_i}{1 + b f_i} \qquad (2a)$$

where V is the polymer volume, $c(f_i)$ is the carbon dioxide concentration in the polymer, and f_i is the gas

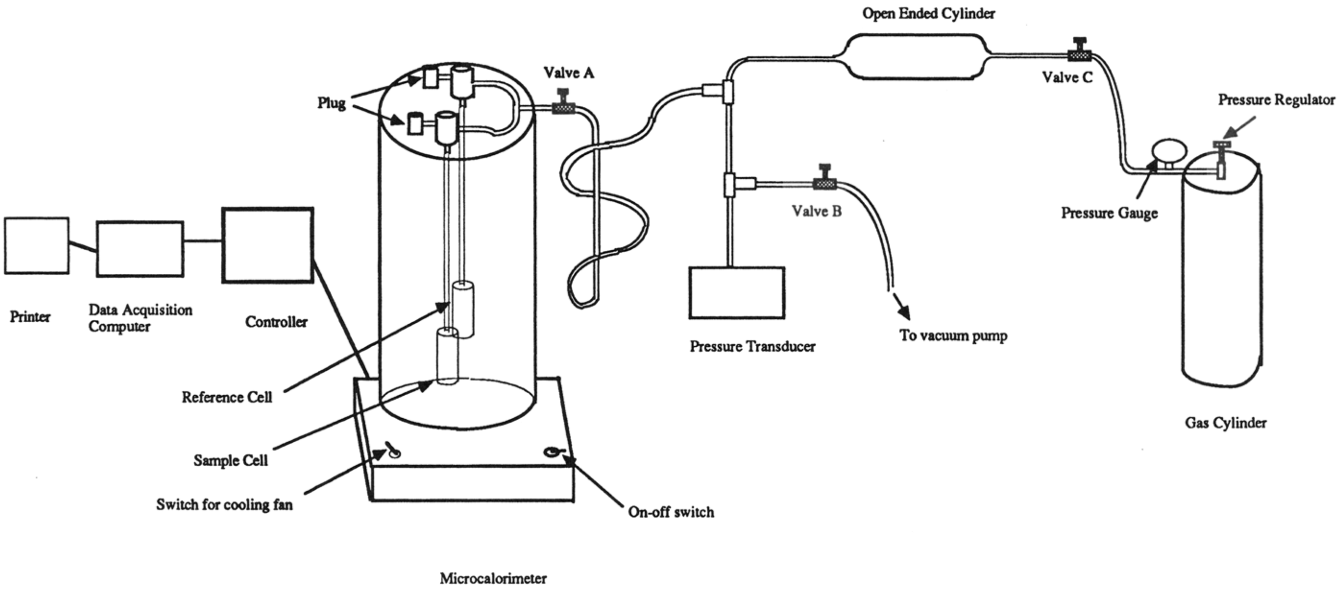

Figure 1. Experimental setup for high-pressure calorimetry.

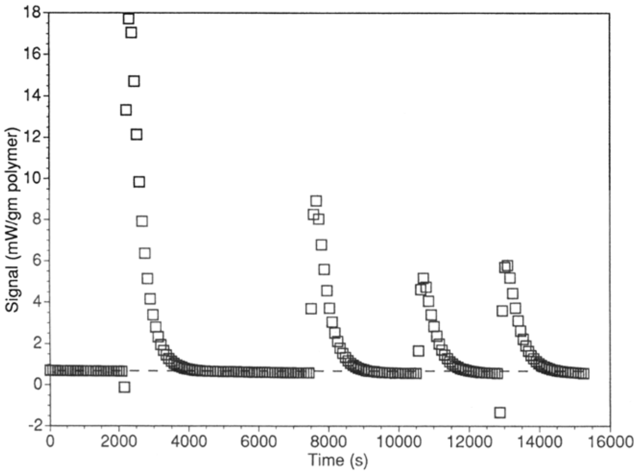

Figure 2. Typical experimental measurements of heat flow as a function of time after a series of pressure increments during a pressurization experiment. The dashed line represents the linear baseline used to compute the total energy change, i.e., the area under the power curve.

Table 2. Values of the Dual Mode Parameters as a Function of Conditioning Pressure and Direction of Pressure Change[22]

conditioning pressure (psia)	direction of pressure change	k_d [(cm³(STP)/cm³)/atm]	b (atm⁻¹)	C'_H (cm³(STP)/cm³)
300	increasing	0.844	0.303	15.16
300	decreasing	0.617	0.285	21.00
600	increasing	0.843	0.265	19.42
600	decreasing	0.254	0.125	46.59
900	increasing	0.868	0.257	21.24
900	decreasing	0.261	0.117	59.50

phase fugacity that corresponds to the pressure p_i. All fugacity calculations were performed using the Soave–Redlich–Kwong equation of state. The dual mode parameters k_d, b, and C'_H are the Henry's law constant, Langmuir affinity constant, and Langmuir capacity, respectively. Values for each were obtained from the literature for carbon dioxide sorption in PC[22] and are tabulated in Table 2. The parameters are strongly dependent on whether the sample is undergoing pressurization or depressurization as well as any conditioning effects through exposure to high-pressure carbon dioxide prior to sorption measurements. A discussion of how carbon dioxide induced free volume changes can lead to these effects is given in the literature.[22]

For PDMS we will use the Flory–Huggins expression to relate N_i to p_i,

$$\ln\left(\frac{p_i}{p_R}\right) = \ln(1 - v_p) + v_p + \chi v_p^2 + V_1\left(\frac{\nu_e}{V_0}\right)\left(v_p^{1/3} - \frac{v_p}{2}\right) \tag{2b}$$

where p_R is an appropriate reference pressure, v_p is the polymer volume fraction, χ is the Flory–Huggins interaction parameter, V_1 is the molar volume of the penetrant, and (ν_e/V_0) is the effective number of moles of cross-links per unit polymer volume in the absence of penetrant. We will use values of 78 atm for p_R, 46 cm³/mol for V_1, and 0.75 for χ, as reported in the literature for carbon dioxide sorption in PDMS.[4] Note that the conditioning effects discussed for sorption in glassy PC are not observed for the rubbery PDMS.

Since $n_i = N_i - N_{i-1}$, one may write the experimentally measured enthalpy change that occurs after the ith pressure change, δH_i, as

$$\delta H_i = (\bar{H}(\text{solid}, p_i) - \bar{H}(\text{gas}, p_i))(N_i - N_{i-1}) \tag{3}$$

where $\bar{H}$ is the partial molar enthalpy of carbon dioxide in either the gas or solid phases. The cumulative enthalpy change after the ith pressure change is given by

$$\Delta H(p_i) = \sum_{j=1}^{i}(\delta H_j + (\overline{\Delta H'}(p_R) - \overline{\Delta H'}(p_j))(N_j - N_{j-1})) = \sum_{j=1}^{i}(\delta H_j + \delta H'_j) \tag{4}$$

where $\overline{\Delta H'}$ is the residual partial molar enthalpy or the difference between the partial molar enthalpy of an ideal gas and carbon dioxide at the same conditions. The residual partial molar enthalpy is calculated from the Soave equation of state,[23] and the reference pressure for the carbon dioxide gas phase is specified as 78 atm, corresponding to the extrapolated vapor pressure at 35 °C.[4]

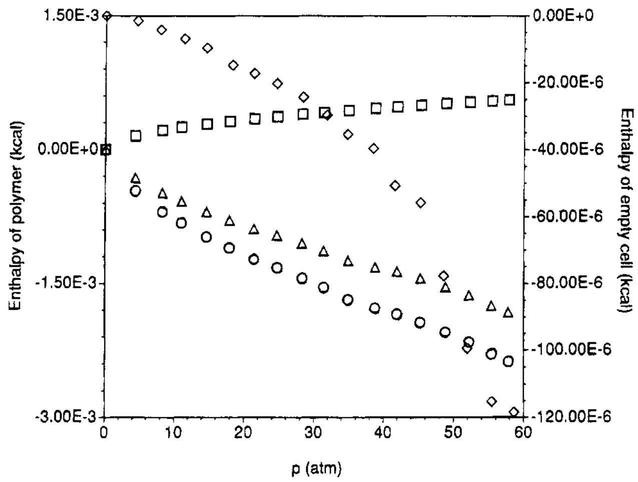

Figure 3. Typical calculated results for sorption in unconditioned PC: cumulative values of the enthalpy change relative to fixed reference states ΔH (triangles), the uncorrected experimental enthalpy change δH (circles), and the enthalpy difference between the reference and experimental gas phases $\delta H'$ (squares). Also shown is the enthalpy change measured with empty cells (diamonds and right hand scale).

The addition of the second term in the sum of (4) converts the experimentally measured enthalpy changes to enthalpy changes relative to a fixed reference gas state at pressure p_R. Neglecting enthalpy changes of the solid phase due to pressure changes, (4) gives the cumulative enthalpy change relative to fixed reference states for both the gas and solid phases. Calculating the enthalpy difference relative to *fixed reference states* allows us to compare the energetics of sorption sites occupied at different gas phase pressures.

However, the enthalpy difference between the sorbed phase and the gas phase at a given experimental pressure or concentration (i.e., omitting $\Delta H'$ in (4)) is the quantity that one should compare to values calculated from the temperature dependence of solubility data using the Clausius–Clapeyron equation.[24,25] This is analogous to use of the Clausius–Clapeyron equation to compute the enthalpy of vaporization. Note that we will report partial molar enthalpies of sorption relative to a *fixed* gas phase reference pressure except for two comparisons to experimental solubility data in the Results and Discussion.

Converting $\Delta H(p)$ to $\Delta H(c(p))$ using (2) allows a simple graphical determination of the partial molar enthalpy of sorption, $\overline{\Delta H}$. The slope of this curve is the isosteric partial molar enthalpy of sorption relative to a fixed gas phase reference state. This quantity is a direct measure of gas–solid interactions.

Results and Discussion

Figure 3 illustrates typical results for ΔH as a function of carbon dioxide concentration, $c(p)$, for an experimental run with a PC sample in which the pressure was increased from a vacuum to the value indicated. Also shown are the cumulative values of δH_j and $\delta H'_j$ which sum to give the cumulative enthalpy. Both the experimental and reference state corrected enthalpy changes are negative, indicating exothermic processes. The residual enthalpy term is positive due to the increase in enthalpy associated with taking carbon dioxide from the reference pressure to the much lower experimental pressures. Furthermore, the residual enthalpy represents approximately 30% of the total enthalpy change.

For comparison purposes, Figure 3 also shows the enthalpy change recorded without a sample; reference and samples cells contain only the insert described previously. Ideally, the enthalpy change should be zero for such an experiment but Figure 3 indicates a small change is observed. We believe this energy change arises from small differences in the volume of the reference and sample cell and the associated differences in pressure–volume work that occur when the pressure is increased. However, the magnitude of the energy change is less than 10% of the experimental measurements and represents a small correction that we will neglect.

As an additional test of the experimental procedure, we used PC samples of varying thicknesses. In addition to the 15 μm thick sample described in the experimental methods section, samples of thickness up to approximately 1 mm were prepared by a combination of film casting and compression molding. The cumulative enthalpy change and associated heat of sorption are constant (less than 10% variation) for sample thicknesses less than 50 μm.

For sample thicknesses greater than 50 μm, the cumulative enthalpy change increases with increasing sample thickness. For the thickest samples, the apparent heat of sorption is *positive*. We attribute this behavior to the dramatic decrease in the mass uptake *rate* and, therefore, the heat release *rate* that occurs in the thicker samples. From the solution to the conservation of mass equation for transient diffusion in a film of finite thickness,[27] one can readily show that the heat release rate drops below the instrument resolution of 1 μW before the total mass uptake approaches 50% of its final value for the thicker samples. The total mass uptake comes to within at least 95% of its maximum value, however, for PC samples less than 50 μm thick. A similar calculation for the PDMS samples gives a maximum useful thickness of over 1000 μm.

Further support for the validity of the thin sample results is provided by comparing the time scales for gas uptake (as given by [sample thickness]^2/[6 × gas diffusion coefficient]) and heat release. The time required to reach composition equilibrium is less than 100 s for samples less than 50 μm thick. This time scale is much shorter than the experimental heat release time of approximately 1500 s. Consequently, the heat of sorption is released almost instantaneously in comparison to the time required for the calorimeter to regain thermal equilibrium. The thermal inertia of the instrument controls the transient heat response, not gas diffusion.

Figure 4 shows the cumulative enthalpy changes measured for sorption in PDMS during pressurization from 0 to 850 psig and subsequent depressurization. The enthalpy changes are exothermic (negative) during pressurization and endothermic (positive) during depressurization. However, for comparison purposes, the depressurization results are given in Figure 4 as the difference between the actual enthalpy change and the cumulative change determined for the entire experiment (i.e., the cumulative heat release calculated after the last pressure decrement in which the sample is evacuated). This difference is negative, and the slope of the curve gives the negative of the heat of desorption, an equivalent heat of sorption measured during desorption. By presenting the data in this manner, one readily visualizes how the heat of sorption differs from the heat of desorption at a given concentration.

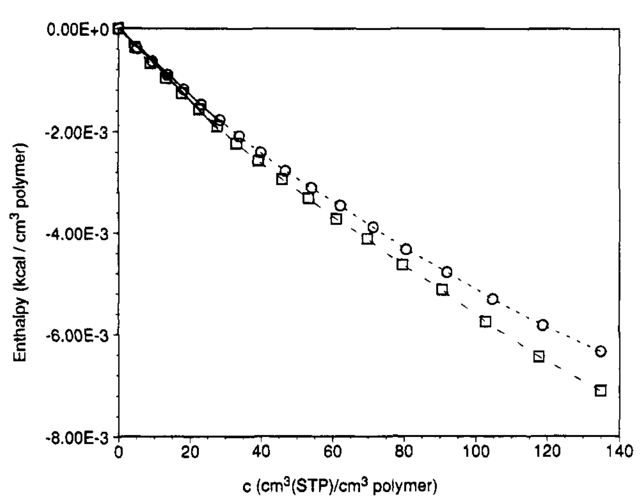

Figure 4. Cumulative enthalpy change for sorption (squares) and desorption (circles) in PDMS over a 0–850 psig pressure range. The solid lines drawn through the data represent the results of a linear regression over the 0–300 psig. The dashed line serves as a guide for the reader.

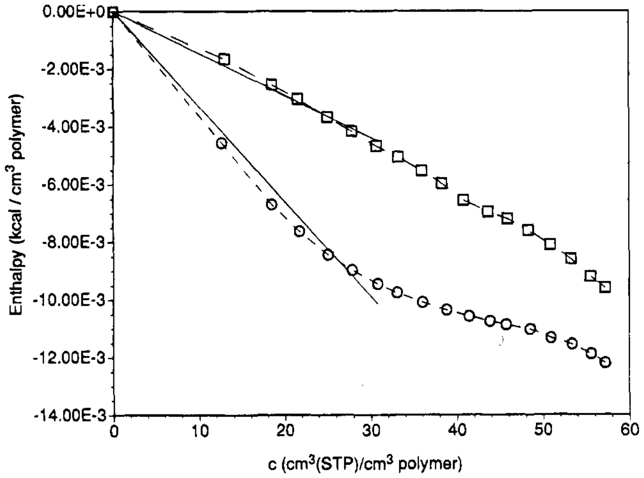

Figure 5. Cumulative enthalpy change for sorption (squares) and desorption (circles) in unconditioned PC over a 0–850 psig pressure range. The solid lines drawn through the data represent the results of a linear regression over the 0–300 psig. The dashed line serves as a guide for the reader.

The two measurements are almost superimposable. The tangent to the curves, the isosteric partial molar enthalpy of sorption, decreases slightly with increasing CO_2 concentration. A linear regression on both curves yields an average heat of sorption from 0 to 300 psig of −1.51 kcal/mol; this decreases to −1.21 kcal/mol if the entire concentration range is considered.

Figure 5 shows the cumulative enthalpy changes measured during pressurization from 0 to 850 psig and subsequent depressurization for an unconditioned PC sample. As observed for PDMS, the pressurization curve is a nearly linear function of concentration over the entire concentration range (up to approximately 850 psig, 60 cm^3(STP)/cm^3 or 0.0027 mol/cm^3 using dual mode model parameters for pressurization of unconditioned polycarbonate). This indicates the partial molar enthalpy of sorption is constant over that concentration range and equal to ∼−3.4 kcal/mol.

The depressurization curve, however, is linear over a much narrower concentration range, from 0 to approximately 30 cm^3(STP)/cm^3 (0.0013 mol/cm^3 or 300 psig using the dual mode model parameters for pressurization of *unconditioned* polycarbonate; we use the unconditioned parameters here because the sample was not held at the highest pressure for the same length of time as that used to obtain the conditioned dual mode parameters given in Table 2; hence, the conditioning histories are different). Furthermore, the equivalent heat of sorption is much larger in magnitude in the low-pressure region, ∼−7.2 kcal/mol instead of −3.4 kcal/mol.

Similar hysteretic behavior is observed in CO_2 permeability, solubility, and apparent partial molar volume in PC for this pressure range.[20–22,29,30] This hysteresis is attributed to subtle changes in molecular conformation and packing in the glassy state induced by CO_2 sorption.

The sorption of a penetrant that greatly swells the glassy matrix, such as CO_2, enhances the rate of polymer segmental motions relative to that in the "equilibrium" glassy state; although a truly equilibrium glassy state does not exist, we will refer to the glassy state prior to conditioning as an "equilibrium" state since the conditioned glassy states age back to this state, as discussed in more detail later. If the penetrant is totally or partially removed over a sufficiently short time scale (the experimental time scale is on the order of 1 h), polymer segments may be trapped in "nonequilibrium" conformations. This conditioning procedure introduces molecular packing defects and increases free volume.

Koros and co-workers argue that most of these new free volume regions are small relative to the molecular size of CO_2 and reduce the effective cohesive energy density of the polymer matrix.[20–22] The reduction in cohesive energy density increases CO_2 solubility and permeability. The additional free volume leads to a concomitant reduction in CO_2 partial molar volume.

These changes are dependent on whether the properties are measured during pressurization or depressurization after exposure to the highest CO_2 gas phase pressure. For example, two different values for CO_2 solubility exist for a single gas phase pressure: one value corresponds to the solubility found upon depressurization from the conditioning pressure, while the other value is the solubility found after complete CO_2 removal and repressurization to the same gas-phase pressure (see Table 2).

These changes are also relatively long lived since glassy relaxation processes govern the approach back to "equilibrium". If the sample is annealed penetrant-free near the glass transition, the permeability and solubility decrease back to their "equilibrium" unconditioned values over a time scale of weeks.[20–22] If the sample is left penetrant-free at ambient conditions, the time scale increases to months. Additionally, if the CO_2 is only partially removed (or even replaced with a gas that does not show hysteretic behavior by itself such as oxygen or nitrogen), the changes in permeability and solubility appear to be semipermanent and might have an impact on membrane-based gas separation applications.[29,30]

To demonstrate the nature and magnitude of conditioning effects, unconditioned samples were tested up to a maximum carbon dioxide pressure of 300 psig. Over this pressure range, the literature indicates the effects of conditioning on solubility are small.[22] Figure 6 shows the cumulative enthalpy changes measured upon pressurization and depressurization. The enthalpy change is linear over the entire concentration range and gives a heat of sorption equal to −3.34 kcal/

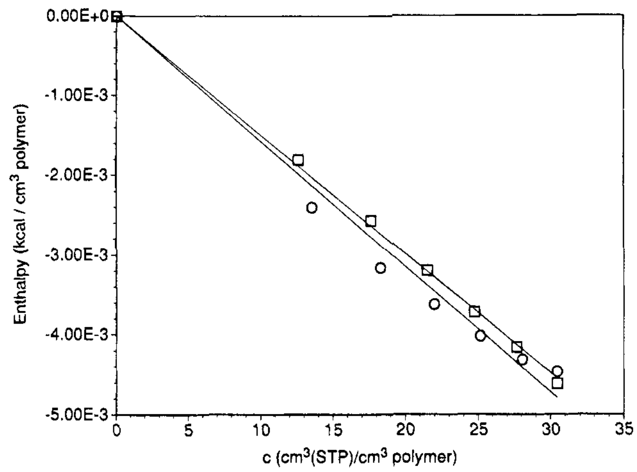

Figure 6. Cumulative enthalpy change for sorption (squares) and desorption (circles) in unconditioned PC over a 0–300 psig pressure range. The lines drawn through the data represent the results of a linear regression.

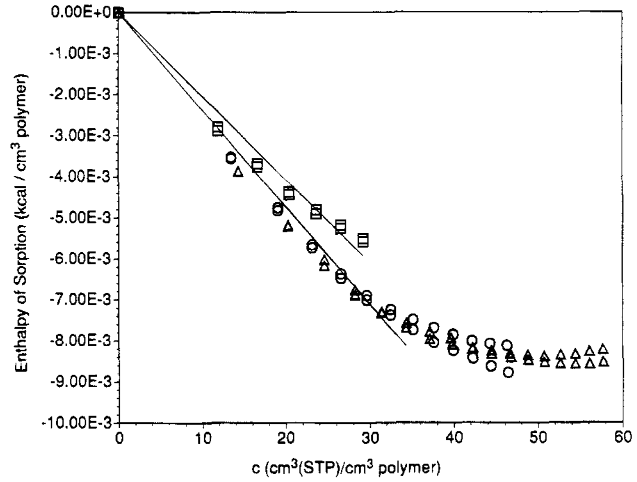

Figure 7. Cumulative enthalpy change for sorption in PC samples conditioned at 300 psig (squares), 600 psig (circles), and 850 psig (triangles). The lines represent the results of a linear regression over the 0–300 psig pressure range. Note results are shown for two independent experimental runs.

mol for pressurization and an equivalent heat of sorption equal to −3.52 kcal/mol for depressurization. The difference between the two values is close to the 4.4% standard deviation of the measurement, as determined from five replicate experiments; the average heat of sorption for these experiments was −3.39 kcal/mol. This suggests that in the absence of conditioning the heat of sorption is independent of concentration.

To further study conditioning effects, polycarbonate samples were conditioned at 300, 600, and 850 psig immediately prior to testing and the highest gas pressure was limited to the conditioning pressure for each sample. The dual mode model parameters for pressurization and depressurization of polycarbonate conditioned at each of these pressures are given in Table 2. Note that the parameters are reported for 300, 600, and 850 psia conditioning pressures (not psig) and that for the sample conditioned at 850 psig we will use the dual mode parameters determined for a conditioning pressure of 900 psia; due to supply pressure limitations we were unable to condition at 900 psia. Figures 7 and 8 show the cumulative heat of sorption (or equivalent heat of sorption) determined during pressurization and depressurization, respectively.

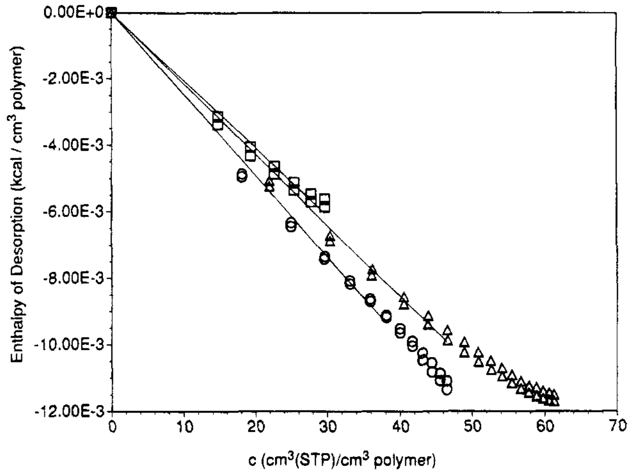

Figure 8. Cumulative enthalpy change for desorpion in PC samples conditioned at 300 psig (squares), 600 psig (circles), and 850 psig (triangles). The lines represent the results of a linear regression over the 0–300 psig pressure range. Note results are shown for two independent experimental runs.

Table 3. Experimental Heats of Sorption and Desorption, Realtive to a Fixed Gas Phase Reference State, as a Function of Conditioning Pressure[a]

conditioning pressure (psig)	heat of sorption (kcal/mol)	heat of desorption (kcal/mol)
300	−4.55	4.57
600	−5.32	5.50
850	−5.30	4.79

[a] Values are the average of two independent measurements and were obtained by a linear regression of the enthalpy change data from 0 to 300 psig.

For the pressurization experiments, the cumulative enthalpy changes are linear only over a narrow concentration range, up to ~30 cm³(STP)/cm³ (0.0013 mol/cm³). The associated constant partial molar enthalpies of sorption are given in Table 3. However, for the depressurization experiments, the cumulative enthalpy changes are linear over a much broader concentration range, up to ~50 cm³(STP)/cm³ (0.0022 mol/cm³). Table 3 indicates that the partial molar enthalpies of sorption and desorption in the low-concentration (or pressure) region differ by less than two standard deviations of the measurement. The difference between the heats of sorption and desorption is largest for the sample conditioned at 850 psig, which shows a 10% difference in magnitude. We will discuss potential sources of this difference later.

The partial molar enthalpy of sorption increases with conditioning pressure. Our interpretation of these changes is similar to that discussed previously for the effects of conditioning on solubility and permeability. Conditioning opens up the glassy polymeric structure by leaving additional free volume after removal of the conditioning gas. This additional free volume is not rapidly eliminated through polymer relaxations at temperatures well below the glass transition temperature for a given CO_2 concentration; note that this temperature decreases as the CO_2 concentration increases.[28]

As the free volume increases, the average spacing between polymer chains must increase. If the spacing was to become comparable to the penetrant molecular size, one would expect sorption to be energetically comparable to condensation. Such an argument is used to justify the large negative heats of sorption obtained from the temperature dependence of the Langmuir affinity constant.[5] Therefore, as the chain spacing

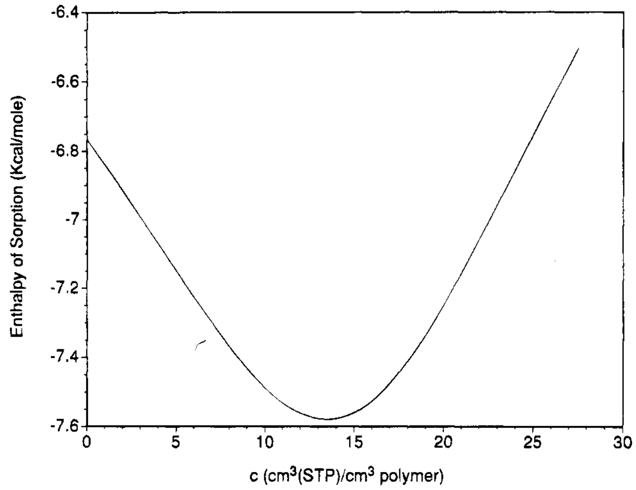

Figure 9. Values of the partial molar enthalpy of sorption computed from the Clausius–Clapeyron equation using the experimental sorption data of Chan and Paul.[24]

Table 4. Experimental Heats of Sorption and Desorption, Relative to the Experimental Gas Phase State, as a Function of Conditioning Pressure[a]

conditioning pressure (psig)	heat of sorption (kcal/mol)	heat of desorption (kcal/mol)
300	−6.00	6.07
600	−6.65	6.87
850	−6.63	6.16

[a] Values are the average of two independent measurements and were obtained by a linear regression of the enthalpy change data from 0 to 300 psig.

increases due to conditioning, one would expect heats of sorption to increase, as observed experimentally.

Figure 9 compares the constant heats of sorption (or desorption) determined in this work to those calculated from the Clausius–Clapeyron equation using the experimental solubility data reported by Chan and Paul.[24] The solubility data were obtained in the 35–75 °C temperature range for PC samples preconditioned at 300 psig for 4 h. One might question the use of this procedure based on equilibrium thermodynamics for nonequilibrium materials such as glassy PC, but the tacit assumption that equilibrium thermodynamics describes the behavior of nonequilibrium materials near a local energy minimum is common in the literature.[18] The apparent heat of sorption varies between approximately −7.5 and −6.5 kcal/mol over the 0–30 $cm^3(STP)/cm^3$ (0–0.0013 mol/cm^3) concentration range. For higher concentrations, one would expect the heat of sorption to approach −4.0 kcal/mol, the van't Hoff energy calculated from the temperature dependence of the Henry's law constant.

As discussed in the Data Analysis, one should compare these values to the partial molar enthalpies of sorption calculated *without* adjusting for the enthalpy difference between the experimental pressure and a reference gas phase pressure. Omitting the $\Delta H'$ term in (4), the heat of sorption for the 300 psig conditioned sample over the 0–300 psig pressure range is constant and equal to −6.1 kcal/mol, which differs by less than 30% from the values in Figure 9. Table 4 summarizes the values of the experimental partial molar enthalpy of sorption relative to the experimental gas phase state (not a fixed reference state) for each of the conditioning pressures considered here.

Somewhat surprisingly, the solubility data give a minimum in the heat of sorption as a function of concentration. We believe this arises from statistical uncertainty in the dual mode parameters rather than some unusual physical phenomena. The fact that the van't Hoff heat of sorption obtained from the Langmuir affinity constant (−4.6 kcal/mol) is comparable to that obtained from the Henry's law constant (−4.0 kcal/mol) supports this hypothesis since the Langmuir affinity constant typically yields values much larger than the Henry's law constant.[5]

One may also compare the results reported here to that of Costello and Koros.[25] On the basis of the temperature dependence of the solubility, they report a heat of sorption of −5.3 kcal/mol for a PC sample without preconditioning or pretreatment for pressures up to ~150 psia. Our measured value of −4.8 kcal/mol, without the fixed gas phase reference pressure adjustment, is in excellent agreement.

On the basis of these observations, we propose the following simple physical picture of the sorption process. Sorbed CO_2 molecules enter pockets of free volume that exist within the glassy polymeric matrix; recent molecular modeling results permit one to visualize these regions.[16] Pockets of sufficient volume to accommodate a molecule may pre-exist, as suggested by dual mode model interpretations of solubility and volume dilation data.[4,5,22] However, some deformation of the polymer matrix is required since the partial molar volume of CO_2 in the sorbed state is always non-zero.[22] The CO_2 partial molar volume increases with concentration, so the required deformation also increases with concentration.

The observations of a constant heat of sorption and desorption and an increasing CO_2 partial molar volume suggest that the work of deformation is a small contribution to the overall heat of sorption over the corresponding CO_2 concentration ranges. The free volume pockets filled by CO_2 molecules may be different sizes but are sufficiently large to make deformation of the glassy matrix a small contribution to the overall energy change. Furthermore, sorption in smaller free volume pockets, where deformation is energetically significant, is either negligible or does not change as a percentage of the total.

Alternatively, these results suggest that one may envision the glassy PC as a low cohesive energy density rubber. The cohesive energy density is much lower than that of a typical rubber because of the excess free volume present in the glassy state. Although the heat of sorption results are consistent with such a simple explanation, the mass uptake and volume dilation measurements are not; the constraints imposed by the finite nature of the excess free volume clearly have an impact and make small molecule sorption in glassy materials a more complex process.

These observations are not consistent with any multisite sorption model in which (1) the heat of sorption varies significantly between sorption sites *and* (2) the fractional occupancy of the sites varies with total concentration. Since our primary objective here is to describe an experimental method for measuring the heat of sorption, we will not present detailed comparisons to the theoretical models discussed in the Introduction but will report on this in a separate communication.

At higher concentrations, the changes in the partial molar enthalpies of sorption and desorption suggest that polymer deformation becomes energetically significant. Additionally, the deformations appear irreversible over the time frame of the experiment, as manifested by the hysteresis in the heats of sorption and desorption measurements as well as in solubility and volume dilation measurements.[22] Interestingly, the changes in the heats of sorption and desorption seem to appear when the partial molar volume of the sorbed CO_2 exceeds ~0.6 cm^3/g, based on the volume dilation results reported by Fleming and Koros.[22]

This physical picture does not provide an explanation of why the heat of sorption is larger in magnitude than the heat of desorption for the 850 psig conditioned sample. We believe this is due to the use of dual mode parameters for a 900 psia conditioning pressure. These parameters overestimate the gas concentrations in samples conditioned at 850 psig, especially for depressurization measurements since the parameters change much more dramatically with conditioning pressure than the parameters for pressurization measurements. The 850 psig parameters would give lower concentrations than the 900 psia parameters for each experimental pressure and would lead to an increase in the magnitude of the partial molar heat of desorption. Thus, one would expect the difference between the magnitude of the heats of sorption and desorption to decrease.

Conclusions

We present direct measurements of the partial molar enthalpy of sorption and desorption of CO_2 in poly(dimethylsiloxane) and polycarbonate. The measurements indicate sorption is a highly exothermic process.

A comparison of the results for the rubbery PDMS and the glassy PC clearly illustrates the differences between the rubbery and glassy states. The heat of sorption is larger in magnitude for the glassy PC than the rubbery PDMS due to excess free volume trapped in the nonequilibrium glassy state. The presence of this excess free volume makes sorption energetically comparable to vapor condensation.

The heat of desorption is equal in magnitude to the heat of sorption for the rubbery PDMS but the two can differ dramatically for the glassy PC in the absence of preconditioning, especially if the desorption measurements are made immediately after the sorption measurements. This hysteresis is due to the introduction of additional excess free volume in the glass during the experiment. As the excess free volume a penetrant can occupy increases, sorption becomes more like vapor condensation.

The differences between the magnitude of the heats of sorption and desorption can be eliminated by preconditioning the sample at the highest experimental pressure. Furthermore, the heat of sorption increases in magnitude with increasing conditioning pressure, indicating a progressively greater "opening up" of the glassy matrix.

The heat of sorption in the glassy PC is independent of concentration in the 0–30 $cm^3(STP)/cm^3$ (0–0.0013 mol/cm^3) range, regardless of sample history. This suggests sorption occurs in energetically equivalent sites in this concentration range. Furthermore, these observations are inconsistent with theoretical analyses of sorption that postulate the presence of multiple, energetically distinct, sorption sites unless the fractional occupancy of each site is independent of total concentration.

For the samples conditioned and tested at the highest pressures, the heat of sorption decreases with increasing concentration. However, the heat of desorption does not change as dramatically. We believe these differences are due to irreversible (over experimental times scales) deformations of the glassy matrix.

When combined with the extensive solubility and volume dilation data available for PDMS and PC, the heat of sorption data reported here provide a detailed characterization of sorption in both a prototypical rubber and glass. Hopefully, this set of data will prove useful in discriminating between alternative theoretical analyses of sorption and ultimately in evaluating new membrane and barrier materials.

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