

Calorimetric probes of carbon dioxide sorption in bisphenol-A based polymers

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We present direct measurements of the partial molar enthalpy of carbon dioxide sorption in a family of structurally related bisphenol-A based polymers. Polymers included in this study are: bisphenol-A polycarbonate, tetramethyl polycarbonate, tetrachloro polycarbonate and tetrabromo polycarbonate. All samples were conditioned at 300 psig prior to measurement. Enthalpy changes were determined using a Setaram C80D microcalorimeter equipped with high pressure cells. The magnitude of the heat of sorption does not correlate well with polymer free volume, gas solubility or gas partial molar volume. However, the values are consistent with heats of sorption calculated from the temperature dependence of solubility. The results suggest that free volume regions are not uniformly accessible; occupation of some free volume regions requires unfavourable deformation of the glassy polymer matrix. The measured heat of sorption represents an energetically weighted average of those free volume regions which are occupied. © 1997 Elsevier Science Ltd.

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INTRODUCTION

One can dramatically alter the transport properties of gases in polymeric materials by modifying the polymer chain architecture. For gas separation membranes, one desires materials that offer a combination of high permeability and selectivity. Unfortunately, the molecular changes that increase permeability often decrease selectivity and vice versa. The 'ideal' polymer would possess high fractional free volume with a narrow free volume distribution peaking at the size of the desired permeating species¹.

Recently, Koros and co-workers^{2,3} identified a pair of structural features, chain packing and chain rigidity, which if changed simultaneously *can* increase both permeability and selectivity. Introduction of bulky substituent groups along the polymer backbone disrupts packing and introduces additional free volume; this increases permeability, but reduces selectivity. Substitution of rigid monomer units or less mobile linkages helps reduce segmental motions along the chain backbone and hence the size of diffusional gaps; this increases selectivity. Alternatively, the introduction of large, *polar* substituents may increase intersegmental interactions, reduce segmental torsional mobility and increase selectivity in an analogous fashion. A combination of these changes can increase both permeability and selectivity.

Muruganandam *et al.*⁴ observed substantial increases in the permeability of CO₂, CH₄, N₂ and He in substituted polycarbonates (PCs) relative to PC. The permeability of

all gases increased three to four times upon symmetric substitution of methyl for hydrogen at the 3- and 5-positions on the bisphenol-A aromatic rings, transforming PC into tetramethyl polycarbonate (TMPC). The authors argue that the increase in permeability is due to the disruptive effect of the methyl on chain packing. The concomitant increase in free volume increases solubility, which in turn increases permeability.

Substituting chlorine, to form tetrachloro polycarbonate (TCPC), leads to a small increase or decrease in permeability relative to PC, while substituting bromine, to form tetrabromo polycarbonate (TBPC), leads to a decrease. These changes arise from an increase in solubility combined with a decrease in diffusivity; for TCPC the net effect is little change in permeability while for TBPC the net effect is a decrease. The authors argue the decrease in diffusivity arises from an increase in cohesive energy density.

Qualitatively, similar changes in material performance occur for many other polymer families upon the addition of bulky substituents or the introduction of rigid monomer units². Furthermore, these studies suggest great potential for further tailoring transport properties by controlling free volume distribution. In particular, materials with a distribution that consists of relatively large free volume regions connected by relatively low free volume regions may offer attractive combinations of permeability and selectivity. One might obtain such a free volume distribution by combining long, flat monomer units with rigid, kinked monomer units containing substituents that disrupt chain packing. In the glassy state, the flat monomer units will attempt to pack

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uniformly (which form the low free volume region), but are prevented from packing too well by the disrupting monomer units (which form the high free volume region). The resulting material behaves very much like a molecular sieve.

The well established dual mode model^{5,6} is commonly used to correlate and interpret gas permeability data. This model postulates that two types of sorption sites exist in the glassy state: Langmuir and Henry's law sites. Langmuir sites are sorption sites that coincide with excess free volume regions present because of the non-equilibrium nature of the glass. Henry's law sites are sorption sites in dense polymer regions. Transport occurs by diffusion in between sorption sites.

Physical interpretation of the dual mode model parameters suggests that gas solubility depends on: excess free volume, gas-polymer interactions and gas critical temperature. Sorption in Henry's law sites increases as the gas-polymer interaction decreases or the gas critical temperature increases. Sorption in Langmuir sites increases as either the excess free volume or the gas critical temperature increases. Significant scatter exists, however, in these general trends. Other probes of the local sorption environment might help resolve some of these discrepancies, especially probes of the gas-polymer interaction, which are generally deduced indirectly from solubility data.

We recently reported direct measurement of the partial molar enthalpy of CO₂ sorption in conditioned and unconditioned PC and poly(di methyl siloxane) (PDMS)⁷. Here, we examine changes in the partial molar enthalpy of sorption in bisphenol-A polymers resulting from systematic changes in primary chain architecture. The results further suggest that free volume distribution is an important factor controlling solubility in these second-generation gas separation membranes.

EXPERIMENTAL

For the enthalpy change measurements we employed a Setaram C80D microcalorimeter (Astra Scientific) equipped with optional high-pressure flow cells. The

instrument has a heat flow sensitivity of approximately 10 μ W and may be operated in either a scanning or isothermal mode. The cells have a volume of approximately 12 ml and an operating pressure range from vacuum up to 1000 psig.

Instrument heat flow and temperature calibrations were checked through scanning measurements of the heat of fusion and fusion temperature of gallium and indium (Aldrich) samples. The melt temperatures of these materials bracket the experimental temperature of 35°C. All results were within 2% of reported literature values⁷.

The inlet ports of the high-pressure flow cells, a sample and reference, were connected to a high pressure CO₂ cylinder ('Bone Dry' CO₂, 99.8% purity, supplied by Wright Brothers) in a manner that allows simultaneous pressurization of both. The outlet ports were closed.

To reduce experimental artifacts due to Joule-Thompson thermal effects, a high pressure reservoir was placed between the gas cylinder and the cells. The gas supplied by the cylinder was depressurized to just above the desired experimental pressure and allowed to reach thermal equilibrium at ambient temperature prior to introduction into the cells. Additionally, sample holders were used to centre samples in the measurement zone, promote good gas contact and make gas flow patterns uniform⁷. Figure 1 illustrates the experimental set up.

The bisphenol-A based polymers studied were: bisphenol-A PC (Aldrich), TMPC (Dow Chemical), TCPC (Dow Chemical) and TBPC (Dow Chemical). To prepare thin film samples, each material was dissolved in methylene chloride (Aldrich) to form a 10% (w/w) solution. The solution was cast on a glass plate using a casting knife (Gardner). The as-cast films were dried under atmospheric conditions for 10–24 h and under vacuum for 24 h. Subsequently, each sample was annealed under vacuum approximately 20°C below the T_g for three days; samples annealed at 10°C above the T_g gave identical results within experimental error. The final film thickness ranged from 10 to 15 μ m. Differential scanning calorimetry showed no detectable crystallinity.

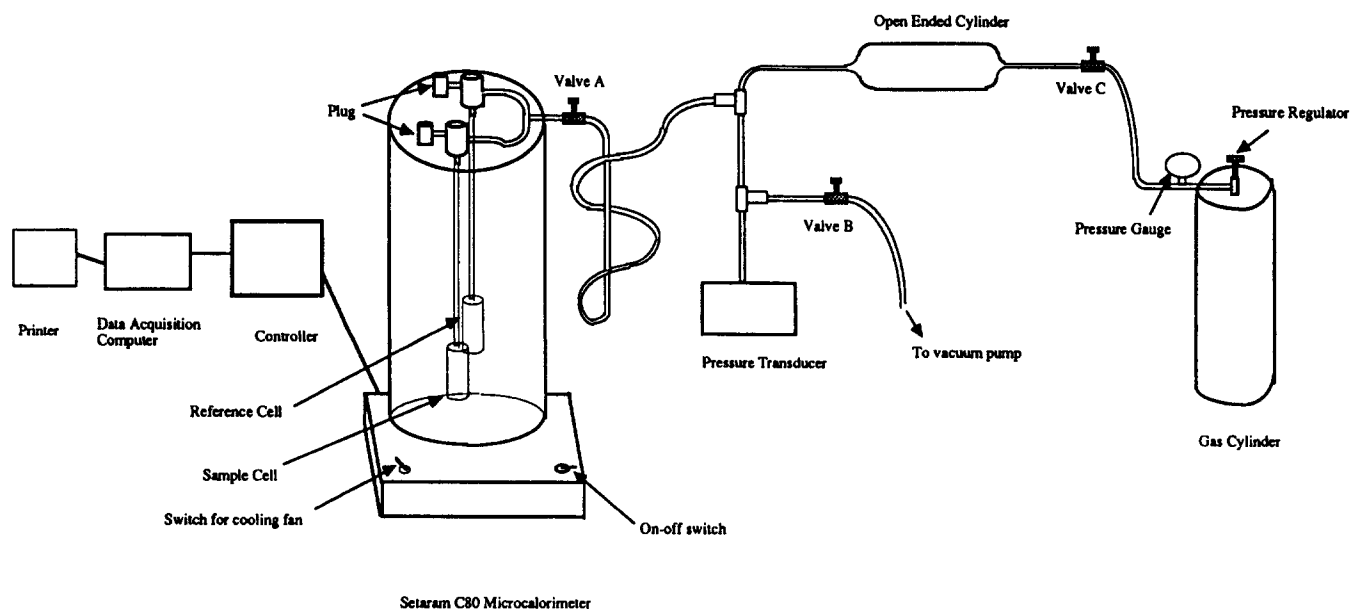


Figure 1 Experimental set up

To start an experimental run, a known mass of polymer film was placed in the sample cell. An equal volume of glass beads was placed in the reference cell to reduce differences in pressure–volume work between the two cells upon changing the gas pressure.

After introducing the sample, the cells were evacuated and held at the experimental temperature of 35°C until a constant thermal baseline was established. To ‘condition’ samples, the CO₂ pressure was increased to 300 psig and held for 24 h; the CO₂ was then removed by applying a vacuum until a new thermal baseline was established.

The gas pressure was increased from vacuum up to approximately 300 psig in increments of 50 psig. The heat flow was allowed to return to the baseline in between pressure increments. Software provided with the calorimeter gave the overall enthalpy change that took place, by integrating the deviation of the heat flow from the baseline with time.

Note that all experiments were conducted isothermally at 35°C. At this temperature, the literature contains a wealth of CO₂ solubility and volumetric data in the materials studied^{3,4,8–13}.

DATA ANALYSIS

The enthalpy change calculated from the raw heat flow data after the *i*th pressure increment (from *p*_{*i*–1} to *p*_{*i*}) is that which accompanies the sorption of *n*_{*i*} molecules of CO₂. One can calculate *n*_{*i*} from the total number of moles sorbed, *N*_{*i*}:

$$n_i = N_i - N_{i-1} \quad (1)$$

For the materials studied here, we will use the dual mode model to calculate *N*_{*i*}:

$$\frac{22\,400N_i}{V} = c(f_i) = k_d f_i + \frac{bC_H' f_i}{1 + b f_i} \quad (2)$$

where *V* is the polymer sample volume, *c*(*f*_{*i*}) is the CO₂ concentration in the polymer, and *f*_{*i*} is the gas phase fugacity that corresponds to the pressure *p*_{*i*}. For all fugacity calculations, we used the Soave–Redlich–Kwong equation of state¹⁴. The dual mode model 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 literature⁴.

One may write the experimentally measured enthalpy change that occurs after the *i*th pressure increment as

$$\delta H_i = [\bar{H}(\text{solid}, p_i) - \bar{H}(\text{gas}, p_i)]n_i \quad (3)$$

where \bar{H} is the partial molar enthalpy of CO₂ in either the gas or solid phases. The cumulative enthalpy change relative to a fixed gas phase pressure, *p*_{*R*}, after the *i*th pressure increment, is given by:

$$\begin{aligned} \Delta H_i &= \sum_{j=1}^i [\delta H_j + (\Delta \bar{H}'(p_R) - \Delta \bar{H}'(p_j))n_j] \\ &= \sum_{j=1}^i [\delta H_j + \delta H_j'] \end{aligned} \quad (4)$$

where $\Delta \bar{H}'$ is the residual partial molar enthalpy which we compute using the Soave equation of state¹⁴. The

second term in the sum in equation (4) (the quantity multiplied by *n*_{*j*}) converts the experimental enthalpy change into an enthalpy change relative to a fixed gas phase state at reference pressure *p*_{*R*}. The reference pressure for the CO₂ gas phase is taken as 78 atm, corresponding to the extrapolated vapour pressure at 35°C. Note that we neglect enthalpy changes of the solid due to pressure changes.

Omitting the second term in the sum in equation (4) gives the cumulative experimental enthalpy change relative to an experimental pressure gas phase reference state. This is the appropriate quantity to compare to enthalpy changes calculated from temperature dependent solubility data using the van’t Hoff or Clausius–Clapeyron relationship.

The enthalpy change, ΔH_i , obtained from equation (4) is plotted *versus* molar concentration, *c*_{*i*}, obtained from equation (2). The slope of this curve is the isosteric partial molar enthalpy of CO₂ sorption relative to the fixed gas phase reference state of 78 atm. We will also present results for sorption relative to an experimental pressure gas phase reference state.

RESULTS AND DISCUSSION

The enthalpy change as a function of CO₂ concentration is shown in *Figure 2* for each of the materials considered in this work. The concentration ranges indicated correspond to pressure ranges of approximately 0–20 atm. Experimental data are shown for two different samples.

Significant curvature exists in the cumulative enthalpy change curve for the substituted materials. Hence, the isosteric heat of sorption (the slope of the curve) changes over the concentration or pressure range of the experiments. The curvature is much less pronounced in PC, as noted in our earlier work⁷.

To assess curvature effects, a cubic expression was fitted to the experimental data, as indicated in *Figure 2*. The isosteric heats of sorption obtained by differentiating this expression with respect to concentration are shown in *Figure 3* for a fixed gas phase reference state of 78 atm and in *Figure 4* for an experimental pressure reference state.

For comparison purposes, values for the fractional free volume (FFV), fractional excess free volume (FEFV), CO₂ solubility at 0 and 20 atm [defined as *c*(*p*)/*p*] and CO₂ partial molar volume at 0 and 20 atm are presented in *Tables 1* and *2*. All values are either taken directly from the literature or calculated from available literature data.

The total free volume is defined as the difference between the occupied volume (the volume occupied primarily by the electron clouds surrounding each atom) and the total volume. The FFV is given by the total free volume divided by the total volume. If the free volume is readily redistributed to facilitate gas sorption, one would expect solubility to increase as the free volume increases (in the absence of specific gas–polymer interactions such as hydrogen bonding). Consequently, FFV values are reported frequently in studies of gas sorption to help interpret changes in solubility data within polymer families. Correlations between FFV and solubility often are weak, though, because portions of the free volume may not be readily redistributed (e.g. interstitial free volume¹⁵).

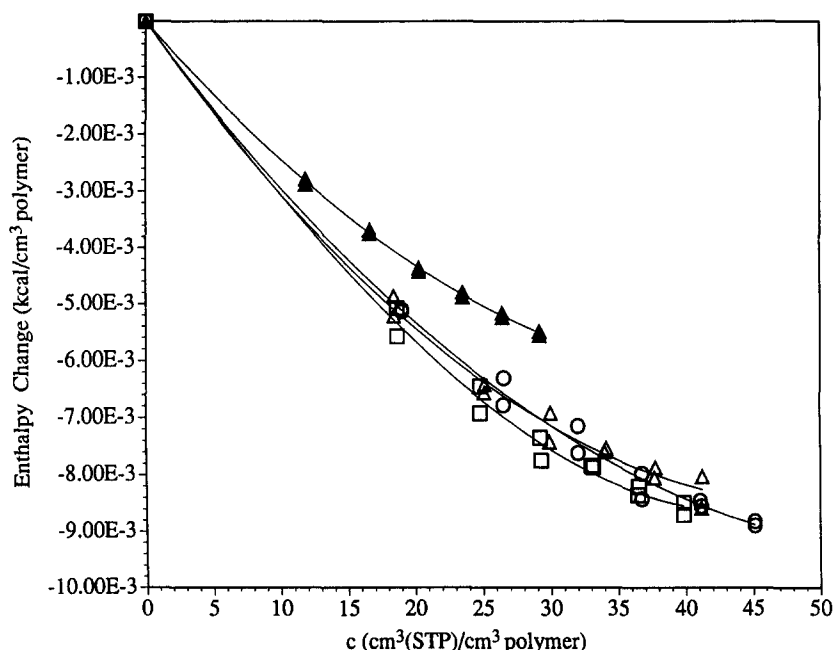


Figure 2 Cumulative enthalpy release as a function of CO₂ concentration relative to a fixed gas phase pressure reference state of 78 atm: (▲) PC; (○) TMPC; (△) TCPC; (□) TBPC. Solid lines indicate the third-order polynomial fit to the data. Results for two samples are shown

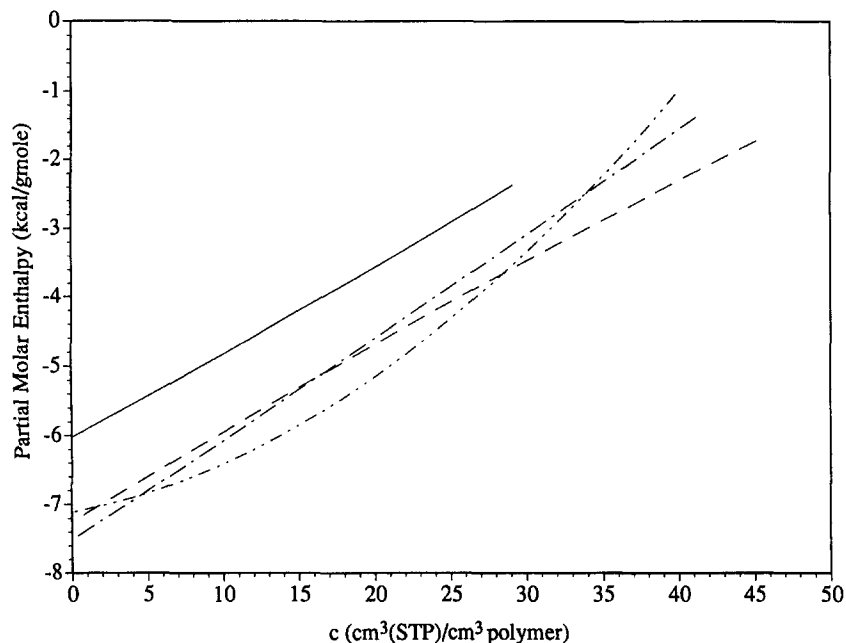


Figure 3 Isosteric heat of sorption as a function of CO₂ concentration relative to a fixed gas phase pressure reference state of 78 atm: (—) PC; (— —) TMPC; (---) TCPC; (- · -) TBPC

The excess free volume contribution to the total free volume is an additional free volume quantity used to help interpret solubility data because of its non-equilibrium nature. The dual mode model is based upon identifying a separate sorption mechanism in these high free energy, free volume regions: gas condensation into a microvoid which is large enough that no deformation of the glassy matrix is required.

The FEFV value in *Table 1* is computed as the difference between the volume of the glass at the experimental temperature and the extrapolated specific volume of a hypothetical liquid at the same temperature

divided by the glass specific volume:

$$FEFV = \left[\frac{\left(\frac{dV}{dT} \right)_l - \left(\frac{dV}{dT} \right)_g}{V_g} \right] (T_g - T) \quad (5)$$

where the subscripts 'l' and 'g' refer to the liquid and glassy states, respectively.

The discussion of the results will focus on two features of these results: the heat of sorption at zero pressure and changes in the heat of sorption with increasing gas

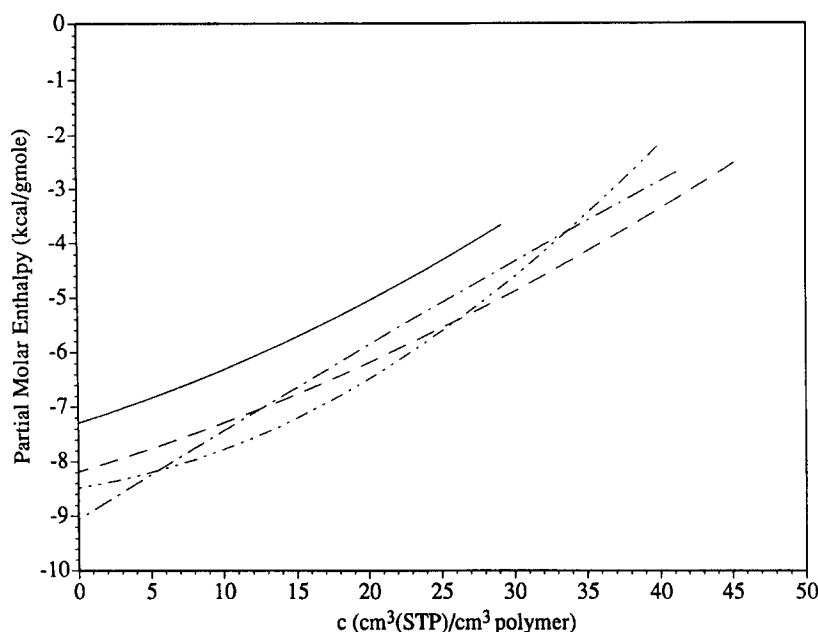


Figure 4 Isotheric heat of sorption as a function of CO₂ concentration relative to an experimental pressure reference state: (—) PC; (---) TMPC; (- · -) TCPC; (· · ·) TBPC

Table 1 Free volume estimates⁴. The value for PC was calculated assuming a 0.15% increase in specific volume relative to an unconditioned sample⁹

Material	Fractional free volume	Fractional excess free volume
PC	0.17	0.051
TMPC	0.18	0.081
TCPC	0.18	0.11
TBPC	0.18	0.12

Table 2 CO₂ solubility and partial molar volume. The partial molar volume values of TMPC are for an unconditioned sample; values for a 300 psig conditioned sample are expected to be smaller

Material	Solubility ^{4,13} (cm ³ (STP) cm ⁻³ atm ⁻¹)		Partial molar volume ¹¹ (cm ³ g ⁻¹)	
	0 atm	20 atm	0 atm	20 atm
PC	5.4	1.5	0.30	0.62
TMPC	8.8	2.2	0.21	0.75
TCPC	9.2	2.0	—	—
TBPC	11	1.9	—	—

pressure or concentration. From *Figure 3* one can see that the magnitudes of the heats of sorption at zero pressure or concentration fall in the following order:

$$\text{TBPC} \sim \text{TCPC} \sim \text{TMPC} > \text{PC}$$

Sorption sites in the three substituted PCs are nearly equivalent energetically and correspond to a lower energy configuration than in PC.

In comparison, the FFVs fall in the order:

$$\text{TBPC} \sim \text{TMPC} \sim \text{TCPC} > \text{PC}$$

while the FEFVs fall in the order:

$$\text{TBPC} > \text{TCPC} > \text{TMPC} \gg \text{PC}$$

FFV values for the substituted materials are nearly identical and much larger than the values for the unsubstituted sample. FEFV values for the substituted

materials are also much larger than for the unsubstituted material, but some variation between the substituted materials exists.

Finally, the solubilities at zero pressure fall in the order:

$$\text{TBPC} > \text{TCPC} \sim \text{TMPC} \gg \text{PC}$$

In the absence of specific gas-polymer interactions, one would expect solubility to increase as either free volume or the magnitude of the heat of sorption increases. The observed results are consistent with this expectation for the relationship between the substituted and unsubstituted materials. The differences between the substituted polycarbonates are relatively small (especially given the uncertainty in the solubility estimates obtained from dual mode model parameters) and we feel do not warrant further discussion here.

At zero pressure, CO₂ partial molar volumes fall in the order:

$$\text{PC} > \text{TMPC}$$

Data for the other materials are not available in the literature. One would expect the partial molar volume to decrease as the magnitude of the heat of sorption increases; sorption into larger free volume regions would decrease the partial molar volume and increase the magnitude of the heat of sorption. These results are consistent with this expectation.

For the three substituted polycarbonates (TMPC, TCPC and TBPC), the magnitude of the isotheric heat of sorption decreases as the CO₂ concentration or pressure increases. Up to pressures of approximately 150 psia, the heats of sorption are very similar for the three materials. At higher pressures, though, the magnitude of the heat of sorption decreases much more rapidly for TCPC and TBPC than for TMPC.

Given the similar heats of sorption (at least up to 150 psia), comparable free volumes and the excess free volume order, one would expect CO₂ solubility in TBPC to remain greater than the solubility in TMPC or TCPC.

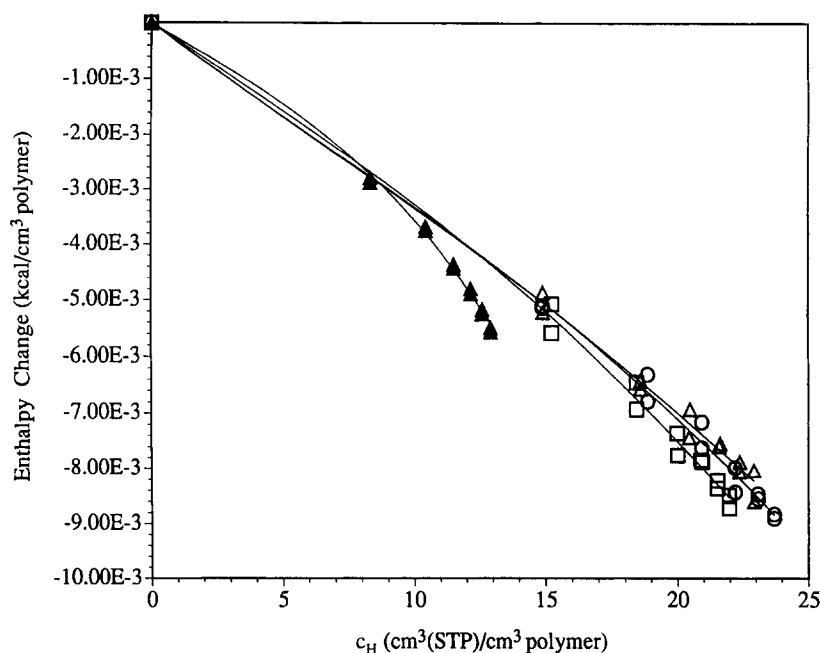


Figure 5 Cumulative enthalpy release as a function of CO₂ concentration in Langmuir sites relative to a fixed gas phase pressure reference state of 78 atm: (▲) PC; (○) TMPC; (△) TCPC; (□) TBPC. Solid lines indicate the third-order polynomial fit to the data. Results for two samples are shown

However, for gas pressures greater than approximately 50 psia, solubilities switch to the following order:

$$\text{TMPC} \gg \text{TCPC} > \text{TBPC}$$

in which TBPC possesses the lowest solubility. One can rationalize such a change by hypothesizing that the free volume in TBPC is not as accessible to sorbing CO₂ molecules as in TMPC or TCPC due to differences in free volume distribution; access to much of the free volume in TBPC requires unfavourable deformation of the polymer matrix.

Such a hypothesis would also explain the observed changes in the heat of sorption at the highest gas concentrations. Above 150 psia, CO₂ has access to more free volume *and* larger free volume increments in TMPC than in either TCPC or TBPC.

To determine if the free volume distribution is nearly bimodal, as suggested by the dual mode model, the cumulative enthalpy changes plotted in *Figure 3* are replotted in *Figure 5* as a function of the gas concentration in the Langmuir regions, c_H . This concentration is given by the second term in the sum in equation (2). One would expect sorption in the Langmuir regions to release much more heat than in the Henry's law regions. Thus, if the Langmuir regions were nearly identical energetically, the cumulative enthalpy change should be proportional to c_H .

The PC data in *Figure 5* show significant curvature. This suggests that the enthalpy change is not a linear function of Langmuir concentration and one cannot capture sorption energetics with a bimodal free volume distribution. The curvature is less pronounced for the substituted materials. This suggests that they possess less variation in free volume distribution than does PC and one can more closely approximate the distribution as bimodal.

One may compare the heat of sorption reported here for PC and TMPC to the values reported by Costello and Koros³ for unconditioned samples. They determined the

heat of sorption from the temperature dependence of the solubility as $-5.3 \text{ kcal mol}^{-1}$ for PC and $-5.1 \text{ kcal mol}^{-1}$ for TMPC. Our measurements bracket these values, and results reported previously for unconditioned PC⁷ are in good agreement with the PC value.

The observed variation in the heat of sorption may impact CO₂ separation processes that utilize these high performance materials. If a CO₂ molecule sorbs into the high pressure side of a TBPC membrane at 300 psia, *Figure 4* indicates that the molecule will release $\sim 2.2 \text{ kcal mol}^{-1}$. However, to desorb from the low pressure side at 0 psia, *Figure 4* indicates that the molecule will require $\sim 8.5 \text{ kcal mol}^{-1}$ of energy. The differences between heats of sorption at 300 psia and desorption at 0 psia are similar for the other substituted polycarbonates.

One can compare these differences in heat of sorption to the enthalpy change associated with Joule-Thompson cooling of the gas. Assuming that CO₂ expands from 300 to 0 psia across the membrane at constant enthalpy, one must supply $\sim 0.2 \text{ kcal mol}^{-1}$ of energy to keep the gas temperature constant. This is much smaller than the difference in sorption enthalpies, $\sim 6 \text{ kcal mol}^{-1}$, for the same pressure difference.

These energetic differences will lead to some cooling of the membrane and contacting gas stream. The extent of cooling will depend on heat transfer rates in the process. As the temperature drops, membrane selectivity will increase, but permeability will decrease. This combination of changes could reduce process capacity.

Note that this thermal effect is superficially similar to thermal effects observed in pervaporation processes¹⁶. However, the thermal effects in pervaporation arise primarily from the heat of vaporization associated with moving a molecule from a liquid to a gas phase. Here, both sides of the membrane contact a gas phase and although there are energetic (Joule-Thompson) differences between the two gas phases the sorption-desorption process itself contributes an additional energy requirement.

The discussion here posits specific differences in free volume distribution to account for the observed heat of sorption, volume dilation and solubility data. As discussed in the Introduction, such differences have been proposed previously to explain variations in gas solubility and permeability in different families of materials² as well as the effects of conditioning⁸⁻¹³.

We are not able to determine or even estimate independently this distribution. However, experimental efforts utilizing small angle X-ray scattering¹⁷, photochromic probes¹⁸ or positron annihilation^{19,20} offer the potential to obtain this information. Ideally, one would make free volume measurements as a function of penetrant concentration to determine the changes that occur as polymer mobility increases with concentration.

These experimental efforts are complemented by recent theoretical efforts to predict free volume distribution and gas solubility using molecular simulations²¹. Molecular models of the glassy state clearly show the complexity of the free volume distribution. The models suggest free volume is present in large clusters connected by low free volume channels in qualitative agreement with experimental measurements. Additionally, the sorption predictions underscore the importance of gas-polymer interactions; predicted isotherms are quite sensitive to the choice of gas-polymer interaction parameters.

Although we are not the first to emphasize the importance of free volume distribution in gas solubility and permeability, we believe the results presented here offer a unique measure of the free volume distribution that can be used to evaluate critically both experimental and theoretical efforts to determine free volume and gas solubility.

CONCLUSIONS

Direct measurements of the heat of sorption of CO₂ in a family of substituted PCs are reported. The results are compared to reported literature values for excess free volume, CO₂ solubility and CO₂ partial molar volume.

For all of the materials examined, the heat of sorption decreases in magnitude with increasing concentration. This suggests that the free volume a sorbing CO₂ molecule occupies decreases as concentration increases. The range of observed values bracket the expected values for PC and TMPC based on temperature dependent solubility data.

The observed variation in heats of sorption between materials can be rationalized in terms of differences in free volume distribution. A comparison of the results for the substituted PCs suggests that the excess free volume in TMPC is much more accessible to sorbing CO₂ molecules than in TCPC or TBPC.

One cannot determine the actual free volume distribution from heat of sorption measurements alone. Like

volumetric change measurements, the heat of sorption measurements represent a weighted average of the free volume distribution. However, we believe the results might be useful in evaluating experimental efforts to measure free volume distribution and theoretical efforts to predict sorption in glassy polymeric materials.

Finally, the results might be useful in evaluating the magnitude of thermal effects on membrane performance. Decreases in the magnitude of the heat of sorption with increasing gas concentration may have a greater effect than Joule-Thompson cooling due to gas expansion in membrane-based gas separation processes.

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