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Dilation of Polymers by Sorption of Carbon Dioxide at Elevated Pressures. 1. Silicone Rubber and Unconditioned Polycarbonate

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ABSTRACT: Mass sorption/desorption and volume expansion/consolidation measurements are reported for silicone rubber and bisphenol A–polycarbonate at 35 °C in the presence of carbon dioxide pressures up to 900 psia. The equipment for the volume dilation measurements is based on direct optical observation of sample dimensions. The dilation data and the sorption data are used to determine the volume change upon mixing and the partial specific volumes of both the gaseous and polymeric materials as functions of pressure. Marked differences are observed for the partial specific volume of carbon dioxide in the rubbery and glassy media. In the rubbery polymer, the partial specific volume of carbon dioxide is similar to its value in low molecular weight solvents and shows little pressure dependence. For glassy polycarbonate, the partial specific volume of carbon dioxide is markedly lower than its value in the rubbery material and shows a much stronger dependence on the external gas pressure. Large hysteresis is also observed in both sorption and volume dilation when comparing the pressurization and depressurization responses of the glassy sample in the presence of carbon dioxide.

Introduction

Significant advances in the thermodynamic understanding of low molecular weight systems have been promoted by the large data base that exists on the phase relationships and volume changes on mixing for these common systems. A smaller but substantial data base also exists for low molecular weight liquids and vapors in polymers. In the case of gas/polymer systems, however, there are very little data for volume changes on mixing.[1,2] Complementary dilation and sorption isotherm data are necessary for a better understanding of gas/polymer thermodynamics to permit rational analysis of this important class of systems.

In order to obtain the volumetric data for gas/polymer systems, a straightforward method of measuring the volume dilation of an unconstrained polymer sample has been developed. Whereas previous studies of gas sorption by our group have dealt with pressures below 30 atm (440 psia), the present study extends measurement capability to 1000 psia for both sorption and dilation.

Isothermal dilatometry measurements indicate that exposure of polycarbonate to carbon dioxide near its critical pressure leads to strong hysteresis in polymer volume and sorption capacity during the sorption/desorption cycle. This response is consistent with related observations for vapor/polymer systems.[3-7] After preswelling a glassy polymer sample with a high activity vapor, exposure to a much lower activity of the same penetrant prevented relaxation in the sorption capacity to the level of the unswollen sample. However, the preswollen matrix relaxed rapidly in the presence of a vacuum to a sorption capacity near its original "as-received" level.[4]

The present study provides additional insight into the phenomenon of penetrant-induced swelling and relaxation. Unlike previous studies utilizing vapors, direct measurement of volume dilation is now possible with the equipment described here. The penetrant used in this study, CO_2, was investigated at a temperature slightly above its critical temperature for pressures extending from zero to slightly below the critical point. The present paper reports results for an unconditioned, as received, sample of polycarbonate. A subsequent paper will describe the rather complex sorption and dilation behavior of a polycarbonate sample following exposure to a high pressure of carbon dioxide prior to characterization.

Background

Sorption in Rubbery Polymers. For low gas concentrations in low molecular weight liquids and rubbery polymers, the concentration of sorbed gas can be described by a Henry's law relationship, where the concentration sorbed is simply proportional to the penetrant pressure.[8]

$$C = k_D p \qquad (1)$$

where C is the concentration of the sorbed gas in cm^3(STP)/cm^3 polymer, k_D is the Henry's law constant in units of cm^3(STP)/(cm^3 polymer atm), and p is the penetrant pressure.

For high-activity vapor/liquid and vapor/rubber systems, higher concentrations of sorbent are observed along with deviations from simple Henry's law behavior. For rubbery polymers, deviations from eq 1 are evident in the form of sorption isotherms that are convex to the pressure axis as penetrant pressure is increased. This convex curvature is normally associated with swelling of the polymer due to the high concentrations sorbed. The Flory–Huggins expression represented by eq 2 provides a satisfactory description of such sorption behavior for high polymers in the absence of strong polymer–penetrant interactions[9]

$$\ln (p/p_0) = \ln (1 - v_p) + v_p + \chi v_p^2 \qquad (2)$$

where p is penetrant pressure, p_0 is the vapor pressure of the penetrant, v_p is the volume fraction of the polymer, and χ is the so-called Flory–Huggins parameter.

Flory has also extended this treatment to describe vapor sorption in cross-linked rubbers[9]

$$\ln (p/p_0) = \ln (1 - v_p) + v_p + \chi v_p^2 + V_1(v_e/V_0)(v_p^{1/3} - v_p/2) \qquad (3)$$

where V_1 is the molar volume of the penetrant, v_e is the effective number of cross-links expressed in moles, and V_0 is the volume of the dry polymer.

Sorption in Glassy Polymers. A popular model used to describe sorption in glassy polymers is the so-called dual-mode sorption model. Inherent in the dual-mode model is the concept of sorption into two idealized environments.[8] One population of sorption (C_D) is viewed as arising from uptake into a dissolved state. This behavior is visualized as being like sorption in rubbery polymers and low molecular weight liquids and is described by Henry's

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law sorption. The second population of sorption (C_H) is viewed as being due to uptake into molecular scale berths or "microvoids" that are present due to the nonequilibrium nature of glassy polymers. This mode of sorption is described by a Langmuir isotherm. The model is represented mathematically by

$$C = C_D + C_H \tag{4a}$$

$$C = k_D p + C_H' bp/(1 + bp) \tag{4b}$$

where k_D is the Henry's law constant in $cm^3(STP)/(cm^3$ polymer atm), b is the Langmuir affinity constant in atm^{-1}, and C_H' is the Langmuir capacity parameter in $cm^3(STP)/cm^3$ polymer.

History Dependence of Glassy Polymer Properties. The history dependence of glassy polymer properties is well documented in terms of thermal,[10-12] mechanical,[13-15] and sorption[3,4,16,17] behavior. Previous studies have related excess enthalpy changes measured by DSC to small-molecule sorption changes,[10,18] but no techniques have existed until recently to observe the actual volume change occurring during the sorption and desorption processes. The after effects on polymer density, gas sorption capacity, and heat capacity caused by preswelling and subsequent removal of CO_2 have been shown to be semipermanent but generally rather small.[17] In certain situations presented below, conditioning effects appear to be large and long-lived and are similar to those observed in some vapor/polymer systems.[3]

Berens and Hopfenberg have developed a technique using polymer microspheres to monitor the time-dependent reductions in the sorption capacity of glassy polymers almost instantaneously following the rapid removal of a preswelling agent.[3,4] This technique, however, is limited to polymers that can be produced in monodisperse submicron microspheres by emulsion polymerization. Moreover, the microsphere technique, while powerful for monitoring sorption capacity, does not permit measurement of complementary volume relaxations during and following preswelling. By the use of microspheres, Berens,[3] Enscore,[5] Connelly,[6] and McCoy[7] have observed long-term hysteretic sorption behavior and report that after preswelling with a high activity vapor, relaxation in sorption capacity is suppressed by a lower activity of the vapor. Berens and Hodge[19] have observed that relaxation in enthalpy is also suppressed by a lower activity of the preswelling penetrant. These effects are generally attributed to the presence of out-of-equilibrium conformations in the polymer introduced during the preswelling process that are inhibited from returning to the previous state by the presence of a small amount of excess penetrant. The detailed processes responsible for the inhibitory responses for both sorption and enthalpy relaxation are not yet well understood.

The use of gases with relatively high critical temperatures and solubilities permits the introduction of large amounts of volumetric swelling at high pressures and allows simultaneous monitoring of volume changes using the equipment developed for this study. This equipment allows monitoring of the dilation during sorption and the consolidation during either desorption or in the penetrant free state following complete desorption.

Materials

The silicone rubber sample used in this study was specially prepared by the General Electric Co., Silicone Products Division. The sample was a 30-mil-thick cross-linked film that had been "postcured" for 4 min at 400 °F. The density of the silicone rubber sample was reported to be 1.10 ± 0.03 g/cm³. A small amount of cross-linking was present in the silicone rubber sample used in this study. To determine the effective cross-link density of the polymer sample, Flory's equation for network systems was employed along with a χ measured by Kuwahara et al.[20] for un-cross-linked dimethylsiloxane in cyclohexane. A dry sample of silicone rubber was first weighed, and then the sample was placed in reagent-grade liquid cyclohexane. Sufficient time was allowed for the system to reach equilibrium and the sample was reweighed. From these measurements the effective molar cross-link density was determined to be $\upsilon_e/V_0 = 1.24 \times 10^{-4}$ g mol/cm³.

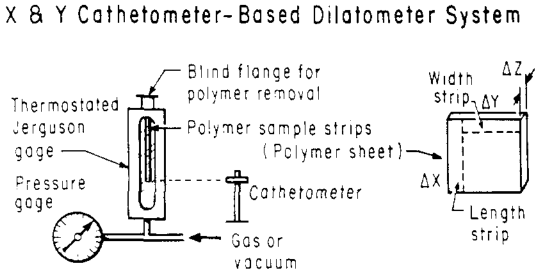

Figure 1. Schematic representation of two-dimensional dilatometer system for high-pressure measurements using polymer film samples.

The polycarbonate sample used in this study was a commercial-grade film, supplied by the General Electric Co. The thickness of the polycarbonate film was approximately 5.0 mil and the density was determined to be 1.200 ± 0.001 g/cm³.

Birefringence measurements showed no measurable orientation for either the polycarbonate or the silicone rubber sample.

The carbon dioxide used in this study was obtained from Linde, Inc., at a purity of 99.99%. The gas was used as-received.

Experimental Section

Gas Sorption Equipment and Procedure. Pure gas sorption measurements were made with a pressure decay cell design that has been successfully used for many years at pressures up to 30 atm (440 psia).[17,18,21] With slight modifications, this design can now be used to make sorption measurements up to 68 atm (1000 psia). The procedure for pure gas sorption measurements up to 68 atm is similar to previously well-established and documented methods for measurements up to 30 atm.[21] In the present study, however, the much higher pressures and sorption levels encountered lead to greater dilation of the polymer sample. This increase in dilation of the polymer necessitates small corrections in the void volume of the sample chamber in the material balance calculations to determine the actual sorption levels. These considerations are presented in a short Appendix to this paper, which is provided as Supplementary Material.

Volume Dilation Equipment and Procedure. A simple method, similar to that used by Ham and co-workers,[22] was used to determine the volume dilation of an unconstrained polymer sample. The equipment allows one to monitor two of the three coordinate dimensions of the sample during sorption and desorption. Any tendency for nonisotropic volume changes can be detected by comparison of the two individually measured dimensions. A schematic of the device for measuring the length, X, and width, Y, dimensional changes is shown in Figure 1. For a typical sample length of 25 cm, the cathetometer permits measurement of changes in length of ±0.01%. In the present study, essentially unoriented sheets were used and isotropic dilation appears to occur.

The procedure for dilation measurements for the X and Y dimensions involves studying strips of polymer cut in the X and Y dimensions of an unoriented sheet. The strips are placed in the Jerguson gage such that they are unconstrained in their ability to elongate but are guided by tracks formed of four steel rods, so the polymer dilates freely in its length dimension but is precluded from curling. After evacuating the sample chamber for approximately 24 h, the undilated sample lengths are determined with the cathetometer. The pressure is then increased in 50 psi steps to 900 psia. At each 50 psi increment, the length of the polymer sample is monitored with a cathetometer until no perceptible length change is observed. Typically 12–24 h is allowed after any perceptible change in length is observed to assure that equilibrium has been achieved. After equilibration at 900 psia,

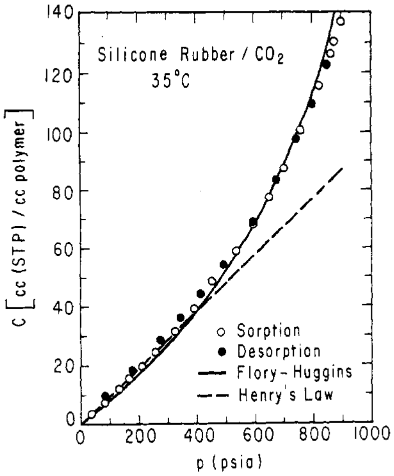

Figure 2. Sorption isotherms for sorption and desorption of carbon dioxide in silicone rubber at 35 °C.

Table I
Partial Molar Volumes of CO_2 in Various Liquids at 25 °C[23,24]

medium	partial molar volume, cm^3/mol
carbon tetrachloride	48.2
chlorobenzene	44.6
benzene	47.9
acetone	44.7
methyl acetate	44.5
methanol	43.0
average	46

the pressure is slowly decreased in 50 psi steps back down to vacuum. In the depressurization cycle, 24–48 h is allowed after any perceptible change in length is observed to assure that no long-term consolidation is occurring.

Results

Silicone Rubber. Figure 2 shows sorption measurements for CO_2 in silicone rubber at 35 °C for pressures up to 900 psia. These data represent the true sorption level corrected for dilation of the sample during the sorption process as described in the Appendix. For pressures up to 300 psia, Figure 2 shows that a Henry's law prediction appears to work quite well in describing the sorption data for CO_2 in silicone rubber. The Henry's law constant for the sorption data below 300 psia is 1.385 cm^3(STP)/(cm^3 polymer atm). The convex curvature of the sorption isotherm at pressures greater than 300 psia is similar to that reported for vapor/polymer systems[4] and is due to the high level of sorbed penetrant. As discussed previously, such vapor/polymer systems are typically described by a Flory–Huggins treatment.

The Flory–Huggins equation, eq 3, may be rearranged to solve for the χ parameter explicitly for a given sorption value. Values for the Flory–Huggins interaction parameter, χ, were determined for each sorption value above 300 psia, and the average value was determined to be $\chi = 0.75$. Also, the volume fraction of polymer was determined from the sorption data, C, by

$$v_p = 1 - v_D = 1 - \frac{CV_1/22415}{CV_1/22415 + 1} \quad (5)$$

where $V_1 = 46$ cm^3/mol was taken as the average of the partial molar volumes of CO_2 in various organic liquids as shown in Table I. Further justification for using this value for the molar volume of CO_2 will be discussed below.

Figure 2 shows the resulting sorption isotherm prediction based on Flory's equation using a constant value of $\chi = 0.75$. The critical temperature (31.2 °C) is slightly lower than the experimental temperature (35 °C), so a value of the vapor pressure, p_0, is undefined at 35 °C. Since the experimental temperature is only slightly greater than the critical temperature, a log–linear extrapolation of the vapor pressure curve to this temperature provides a reasonable estimate of p_0 used in calculating the activity in eq 3. The extrapolated value of the vapor pressure at 35 °C was determined to be 78 atm. Also, at pressures as high as 900 psia the behavior of CO_2 is highly nonideal, and the expression for the activity of CO_2, $a = p/p_0$, as shown in eq 3, is not rigorously followed. The activity should be expressed as $a = f/f_0$, however, Figure 2 shows that the Flory–Huggins equation, written as shown in eq 3, is still quite effective for describing the behavior of highly sorbing gases such as CO_2 in rubbery polymers.

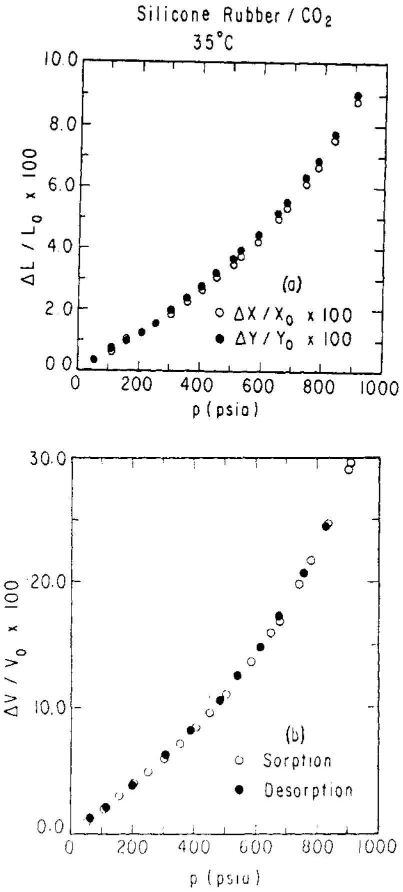

Figure 3. (a) Dilation of the X and Y dimensions of a 30-mil-thick silicone rubber sample at 35 °C as a function of external carbon dioxide pressure. (b) Calculated isotropic volume dilation of the silicone rubber sample using the average of the two linear dilation measurements shown in (a).

Figure 3a shows length dilation measurements for two dimensions of a silicone rubber sample at 35 °C and pressures up to 900 psia. The data in Figure 3a indicate that the percentage dilation for the X and Y dimensions of the unoriented film are essentially equivalent. On the basis of the similarity in dilation for the two dimensions, the assumption of isotropic swelling is reasonable. If one calculates the isotropic dilation corresponding to the average of the dimensional changes in Figure 3a, the resulting volume dilation is shown in Figure 3b.

With complementary sorption and dilation data, thermodynamic analysis of the system is straightforward to determine the partial specific volumes of the polymer and the penetrant. Shown in Figure 4a is a plot of the specific volume of the penetrant-laden polymer vs. the mass fraction of CO_2. The partial specific volumes of the polymer and penetrant can be determined graphically from

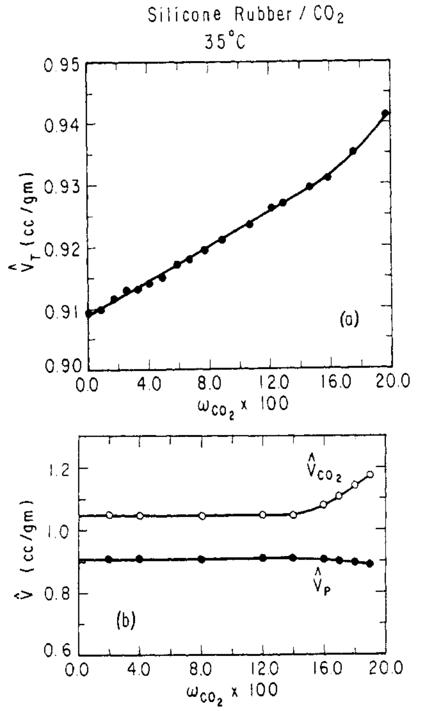

Figure 4. (a) Total specific volume of the penetrant-laden silicone rubber sample as a function of carbon dioxide mass fraction. (b) Partial specific volume of silicone rubber and carbon dioxide as a function of carbon dioxide mass fraction.

the tangential slope of the specific volume versus mass fraction plot in Figure 4a. The partial specific volumes of the polymer and penetrant are shown in Figure 4b as a function of mass fraction. Figure 4b indicates that the partial specific volumes for the polymer and penetrant are essentially independent of mass fraction below a mass fraction of 14%. For mass fractions higher than 14% there is a slight upswing in the partial specific volume of the penetrant-laden polymer that is similar to "equation of state" effects observed for carbon dioxide/butane mixtures near the critical point.[25] The "equation of state" effect refers to enhanced dilation of a supercritical component relative to a subcritical component in a mixture as the critical region is approached.

Rubbery polymers are equilibrium solids, and the interactions of gases with rubbery polymers and low molecular weight liquids have been shown to be very similar.[26] The infinite dilution partial molar volumes for CO_2 in various low molecular weight liquids shown in Table I[23,24] are rather insensitive to the type of medium and decrease only slightly as interactions between the medium and CO_2 increase. The average of the partial molar volumes for the solvents at infinite dilution at 25 °C is approximately 46 cm^3/mol. The partial specific volume for CO_2 in the swollen silicone rubber is essentially constant at 1.05 cm^3/g, corresponding to a partial molar volume of 46.2 cm^3/mol. Hirose and co-workers[2] have measured the partial molar volume for CO_2 in low-density polyethylene over a temperature range of 25 to 55 °C and observed no strong temperaure dependence for the partial molar volume of the sorbed CO_2. The average molar volume Hirose measured for the polyethylene/CO_2 system in the temperature range 25–55 °C was 44.5 cm^3/mol, in good agreement with the present values in silicone rubber. Thus, the behavior of CO_2 in different rubbery polymers and low molecular weight liquid media appears to be very similar near room temperature.

Polycarbonate. Figure 5 shows sorption measurements for CO_2 in an "as-received" polycarbonate sample and compares the sorption values with a model prediction by using the following dual-mode parameters determined by Koros et al.[27] for a different polycarbonate sample exposed to only 350 psia: $k_D = 0.685$ $cm^3(STP)/(cm^3$ polymer atm), $b = 0.262$ atm^{-1}, and $C_H' = 18.805$ $cm^3(STP)/(cm^3$ polymer). The history of the present sample and the sample for which the model parameters were determined are different, so it is not surprising that some difference is observed in the sorption behavior of the two samples. Nevertheless, it is satisfying that the simple dual-mode sorption model [eq 4b] describes the current data up to 900 psia reasonably well with model parameters fit over the range up to only 350 psia. As with silicone rubber, a correction for the increase in polymer volume has been accounted for in the sorption calculations for CO_2 in polycarbonate, and the magnitude of this correction is discussed in the Appendix. As noted earlier, measurements are currently under way to determine the conditioning effect observed after removing the CO_2 and repeating the sorption measurements. These effects will be discussed in a later paper.

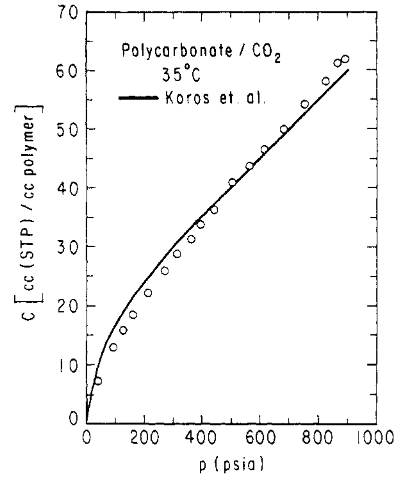

Figure 5. Sorption isotherm for carbon dioxide in polycarbonate at 35 °C. The circles are the experimental data from this study, and the line is calculated from eq 4b using the dual-mode sorption parameters reported earlier for a different sample.[27]

Figure 6a shows length dilation measurements for CO_2 in a 5.0-mil polycarbonate film. The polycarbonate used in this study was unoriented and measurements in Figure 6a show that percentage dilations for the X and Y dimensions are essentially equivalent. Due to the similarity in the dilation for the two dimensions, the assumption of isotropic swelling is probably again satisfactory. Figure 6b shows the isotropic volume dilation corresponding to the average of the dimensional changes in Figure 6a.

With the sorption data in Figure 5 and the dilation data in Figure 6b, the specific volume of the penetrant-laden polymer was determined as a function of CO_2 mass fraction as shown in Figure 7a. As in the case of the silicone rubber system, one can then determine the partial specific volumes of the penetrant and polymer graphically with standard thermodynamic techniques based on intercepts of the tangents of the volumetric data in Figure 7a. The partial specific volumes for CO_2 and the polymer are shown in Figure 7b. The infinite dilution partial specific volume of CO_2 in polycarbonate is approximately 0.41 cm^3/g (or 17.9 cm^3/mol), which is about *61% smaller* than for CO_2 in similar low molecular weight liquid and rubbery polymer environments. The partial molar volume increases as the amount of CO_2 sorbed into the polymer increases, but even at a CO_2 weight fraction of 8.0% the partial molar volume is still 22% lower than the partial molar volume of CO_2

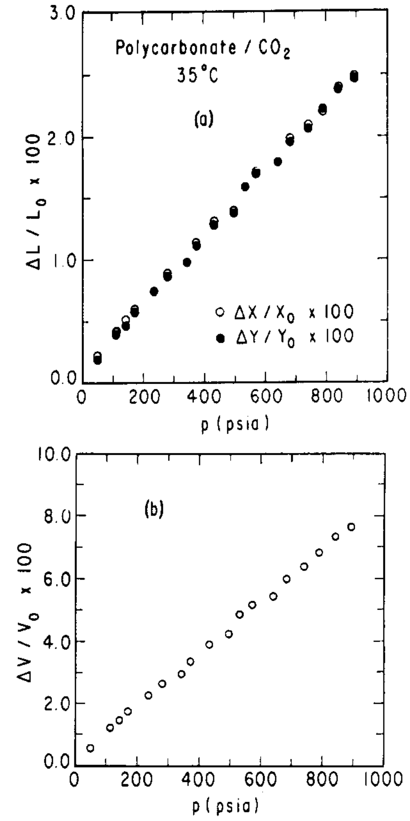

Figure 6. (a) Dilation of the X and Y dimensions of a 5-mil-thick polycarbonate sample at 35 °C as a function of external carbon dioxide pressure. (b) Calculated isotropic volume dilation of the polycarbonate sample using the average of the two linear dilation measurements shown in (a).

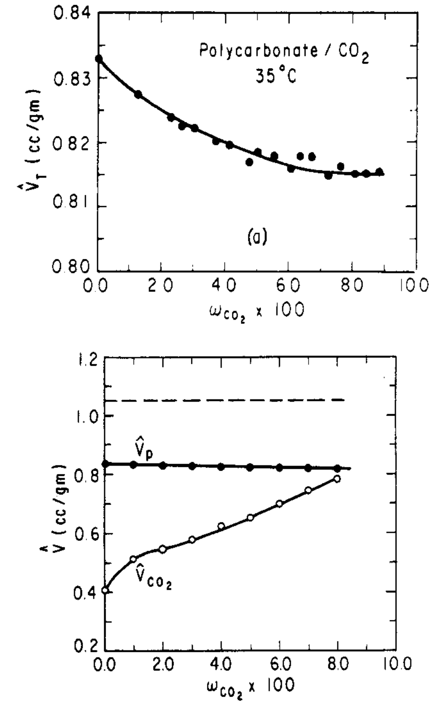

Figure 7. (a) Total specific volume of the penetrant-laden polycarbonate sample as a function of carbon dioxide mass fraction. (b) Partial specific volume of polycarbonate and carbon dioxide as a function of carbon dioxide mass fraction. The dashed line represents the infinite dilution partial specific volume for carbon dioxide in liquids and silicone rubber.

in low molecular weight systems.

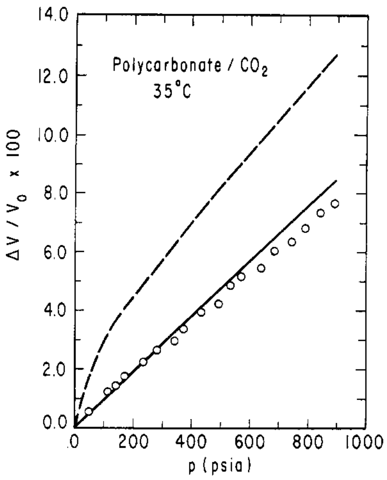

Figure 8. Comparison between predictions of eq 6 and eq 7 for isotropic volume dilation caused by sorption of carbon dioxide in polycarbonate. The points are the actual dilation data from Figure 6b.

The extraordinarily low value of the infinite dilution CO_2 partial molar volume and the strong compositional dependency in glassy polycarbonate can be physically rationalized with the concept of molecular-scale gap-filling implicit in the so-called dual-mode sorption model represented by eq 4.[27-30] This model accommodates the fact that glassy polymers are nonequilibrium solids whose state is dependent upon the excess volume and enthalpy in the material. One can consider the excess volume in glassy polymers, distributed as molecular- and submolecular-scale gaps, to provide additional sorption capacity over and above the normal sorption mode typical of liquid and rubbery polymer environments.[28] The dual-mode viewpoint suggests that ideally only the fraction of the total sorption associated with the actual separation of chain segments to accommodate penetrant will cause volume dilation, this situation clearly gives rise to an apparent reduction in the infinite dilution partial molar volume of CO_2 in the glassy polymer system compared to low molecular weight systems in which such a gap-filling mechanism does not occur.

If the Langmuir sorption term in the dual-mode sorption model corresponds to a true hole-filling process, the volume dilation relative to V_0, the unswollen polymer volume, is predictable in terms of the fraction of CO_2 sorbed according to the linear sorption term $k_D p$ in eq 4. If one uses the average value of V_{CO_2} = 46 cm^3/mol for the partial molar volume of CO_2 from Table I and assumes this volume is approximately constant and also applies to the polymer state at 35 °C, one can predict the volume dilation based on either the total penetrant concentration, C_T, or based only on the dissolved concentration, C_D, as shown in eq 6 and 7, respectively. The volume dilation predictions are shown in Figure 8 as the dashed line for eq 6 and the solid line for eq 7. The data points in Figure 8 appear to agree quite well with the prediction based on swelling due only to the Henry's law fraction of the total sorption population (eq 7). This observation supports the physical interpretation of the dual-mode model and suggests that unification of the theoretical understanding may be possible for gases sorbing in low molecular weight liquids, rubbery polymers, and glassy polymers.

$$\frac{\Delta V}{V_0} = \left(k_D p + \frac{C_H' b p}{1 + b p}\right)\frac{V_{CO_2}}{22415} \tag{6}$$

$$\frac{\Delta V}{V_0} = k_D p \frac{V_{CO_2}}{22415} \tag{7}$$

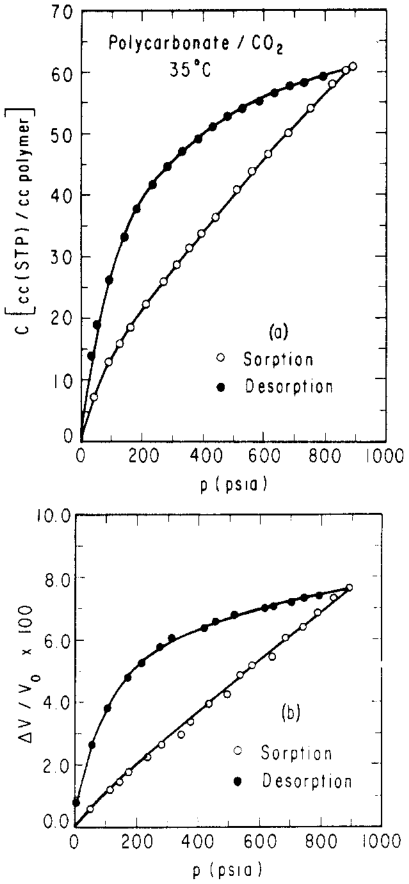

Figure 9. (a) Sorption/desorption data illustrating the pronounced hysteretic response observed in the carbon dioxide/polycarbonate system at 35 °C. (b) Volume dilation and consolidation data confirming the pronounced hysteretic response observed in the carbon dioxide/polycarbonate system in (a).

Hysteretic Behavior. As shown in Figure 9, after slow pressurization and equilibration of the polycarbonate sample at a CO_2 pressure of approximately 900 psia, a systematic desorption was followed down to zero pressure. A hysteretic response was observed when compared to the sorption process. In all cases for the sorption and desorption cycles, extremely long equilibration times were permitted. To ensure that no long term changes were occurring, typically 24–48 h was allowed after any perceptible polymer length change in the dilatometer or pressure change in the sorption cell had ceased. In one case for volume dilation during desorption, the pressure was maintained for more than 5 days at 500 psia without any significant relaxation in volume. Also in the pressure decay cell during desorption, the pressure was virtually unchanged at 500 psia for 16 days. (A 1.0% decrease in sorption level was observed from day 2 to day 16.) Consequently, the hysteretic behavior appears to be characteristic of two semipermanent states existing at the same external penetrant pressure. In fact, the hysteretic values for the sorption and desorption isotherms may be undergoing an extremely slow change toward a unique equilibrium state that requires a much longer period than the current experimental time scale to observe. The data in Figure 9 show clearly that the sorption/desorption responses mimic the volume dilation curve's hysteresis. As noted earlier, previous investigators have observed a hysteretic response in sorption capacity, but the present data are the first to show complementary sorption and volume hysteresis for CO_2 in polycarbonate. Kamiya has measured a similar hysteretic sorption behavior for CO_2 in polycarbonate and polysulfone up to 50 atm[31] and has measured hysteretic behavior in volume for sorption/desorption of CO_2 in polysulfone and poly(ethylene terephthalate).[1]

Wonders[17] reported that after conditioning a sample at 60 atm with CO_2, subsequent sorption experiments showed higher values of penetrant uptake than a sample conditioned at 20 atm. However, the changes in sorption level after total removal of the CO_2 and repressurization with CO_2, as measured by Wonders, is much less than the magnitude of the hysteretic differences between the sorption and desorption values at 20 atm (300 psia) shown in Figure 9a. Density measurements by Wonders showed a small increase in volume for the sample conditioned at 60 atm, and the increase in sorption capacity was attributed primarily to an increase in the unrelaxed volume in the sample. In terms of the dual-mode model, an increase in sorption capacity in unrelaxed sites may be described by an increase in the Langmuir capacity parameter C_H'. Consistent with this interpretation, the dilation data in Figure 9b show that at the zero pressure limit a small amount of unrelaxed volume remains in the polymer even after complete removal of CO_2 (24 h under vacuum). This unrelaxed volume can be related to an increase in the Langmuir capacity by[28]

$$\Delta C_H' = \left(\frac{\Delta V}{V_0}\right)\rho^*_{CO_2} \tag{8}$$

The parameter $\rho^*_{CO_2} = 1/49$ mol/cm³ corresponds to the effective molar density of CO_2 in a microvoid environment estimated from data in the Zeolite literature.[32] Using the values for $\Delta V/V_0$ for the conditioned polymer, one predicts $\Delta C_H' = 3.7$ cm³(STP)/cm³ polymer. This is in good agreement with the value of $\Delta C_H' = 4.2$ cm³(STP)/cm³ polymer reported by Wonders.[17]

Conclusions

Sorption of carbon dioxide in silicone rubber can be described satisfactorily for pressures up to 900 psia with the simple Flory–Huggins theory, as has been applied by others to a number of vapor/polymer systems. The partial specific volumes for carbon dioxide and polymer in this system are relatively constant up to the critical pressure for carbon dioxide. The partial specific volume of CO_2 in silicone rubber is similar to values reported in low molecular weight solvents. This fact substantiates the concept that gas sorption behavior is similar in rubbery polymers and simple viscous liquids. The lack of volume and sorption hysteresis during pressurization and depressurization of the rubbery sample with CO_2 also supports prevailing views of the basic equilibrium nature of the rubbery state with respect to time scales typically encountered in sorption and transport applications.

Markedly different responses were observed for CO_2 interactions with the glassy polycarbonate sample compared to the rubbery silicone sample mentioned above. The simple dual-mode sorption model, using parameters fit to data at pressures less than 350 psia, is effective for describing mass uptake at pressures up to 900 psia for the CO_2/polycarbonate system. Partial specific volumes of CO_2 are much lower and much more dependent on the external gas pressure in the case of the glassy polymer than in the case of the rubbery polymer. The dual-mode model is based on the concept of the existence of excess unrelaxed volume in the nonequilibrium glassy state. This model has been shown to be effective for explaining the observed low values for the partial specific volumes for CO_2 in polycarbonate. The idealized notion that only the so-called "dissolved" fraction of the total sorbed population con-

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tributes to dilation offers a means of unifying the thermodynamic description of gas sorption in low molecular weight solvents, rubbery polymers, and glassy polymers. That is, if account is taken for the amount of unrelaxed volume separating a glassy polymer from a true equilibrium material, it appears that the sorption and dilation behavior of gases in glassy polymers is understandably different from the behavior of gases sorbed into an equilibrium material.

Marked hysteresis is observed in the volume and sorption level for pressurization and depressurization with CO_2 for the case of polycarbonate. This behavior suggests that during depressurization the presence of CO_2 retards relaxation of the polymer to its former thermodynamic state observed during pressurization. These observations are consistent with the behavior reported by others for vapor/polymer systems.

Finally, the unrelaxed volume present in a glassy sample following complete removal of CO_2 appears to be directly assignable to increases in the Langmuir sorption capacity. The unrelaxed volume present in the sample after complete removal of CO_2 correlates very well with an increase in sorption capacity measured for a polymer sample with a similar history.

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Registry No. CO_2, 630-08-0; bisphenol A polycarbonate (SRU), 24936-68-3; (bisphenol A)·(carbonic acid) (copolymer), 25037-45-0.

Supplementary Material Available: Appendix detailing the effect of volume correction on sorption values for carbon dioxide in silicone rubber and polycarbonate (Figures A-1 and A-2) (5 pages). Ordering information is given on any current masthead page.

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Location of the Adhesion Promoter (γ-Aminopropyl)trimethoxysilane in a Cured Silicone RTV Matrix

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ABSTRACT: Secondary ion mass spectrometry (SIMS) depth profiling has been used to determine the location of (γ-aminopropyl)trimethoxysilane (GAP) in both silica-filled and unfilled silicone RTV elastomers. The adhesion promoter, $NH_2CD_2CH_xD_{2-x}CH_2Si(OMe)_3$, was found to be uniformly distributed throughout the matrix with no apparent increase at either the air– or metal–substrate interface. No adhesion was found in materials without adhesion promoters, which suggests that a minimum concentration at the surface is necessary for adhesion; however, this concentration is not greater than that found in the bulk.

A typical RTV composition contains reactive end-stopped polymer, cross-linker, filler, catalyst, and adhesion promoter. In most cases, the adhesion promoter is an organofunctional trialkoxysilane such as (methacryloxopropyl)trimethoxysilane or (aminopropyl)trimethoxysilane. Unfortunately, the mechanism of adhesion to substrates induced by these silanes is poorly understood. Two roles for the adhesion promoter may be envisioned. First, the

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