Isosteric heat of sorption of CO_2 in poly(ethylene terephthalate)

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(Received 28 January 1985; revised 25 April 1985)

Sorption isotherms for carbon dioxide in poly(ethylene terephthalate) have been measured at 35–55°C. The isotherms were measured gravimetrically on a Mettler Thermoanalyzer-1 from vacuum to 1 atmosphere. The sorption data were used to generate sorption isotherms from which the isosteric heat of sorption of CO_2 in PET was determined. At 45°C the isosteric heat of sorption increases from -10 kcal/mole at a concentration of 0.5 cm^3 (STP)/cm^3 (polymer) to -8 kcal $mole^{-1}$ at a concentration of 1.5 cm^3 (STP)/cm^3 (polymer). It has been reported in the literature that the isosteric heat of sorption for this system decreased through a minimum before increasing with increasing concentration. Our measurement of the low-pressure sorption isotherms shows that this is not the case.

(Keywords: poly(ethylene terephthalate); carbon dioxide; sorption; isosteric heat; dual-mode model)

INTRODUCTION

As part of an extensive study on gas sorption in glassy polymers, Koros, Paul and Huvard derived an expression for the isosteric heat of sorption based on the dual-sorption–mobility model[1]. According to this analysis, the isoteric heat of sorption decreases through a minimum before finally increasing with increasing gas concentration. The minimum occurs at a concentration near the value of the Langmuir capacity coefficient (C'_H). No satisfying physical arguments have been presented to account for the presence of the minimum. In support of the dual-mode interpretation, Koros *et al.* reported that the slopes of the sorption isosteres showed a minimum coincident with the minimum predicted by the dual-mode formalism. Unfortunately, the isosteres at low concentrations, which characterizes the region of the minimum in the ΔH_I curve, were derived by extrapolating the concentration vs. pressure curves to concentrations well below those of the original data set. Thus, there has been no real test of the applicability of the dual-mode model to the description of the isosteric heat of sorption.

We report here measurement of sorption isotherms for CO_2 in PET at low pressures. We then use a model independent method to calculate ΔH_I in order to determine the slope of the ΔH_I vs. concentration curve at low concentrations.

EXPERIMENTAL

A powdered sample of poly(ethylene terephthalate) (Goodyear Tire and Rubber Co., lot no. VFR1625A) was prepared by first dissolving the polymer in a solvent consisting of 2 parts of 1,1,2,2-tetrachloroethane and 1 part phenol followed by precipitation in excess methanol. Residual phenol was removed with chloroform in a Soxhlet extractor. Residual phenol was assumed to be less than 0.1% as none could be detected in the purified sample of PET by either mass spectrometry or *FT*i.r. The powder used in the sorption measurements had a surface area of 7.5 m^2 g^{-1}. X-ray diffraction analysis using the procedure of Statton[2] indicated 34% crystallinity in the sample. The T_g of the sample was 67°C.

In preparation for the sorption measurements the PET sample was conditioned[3] by exposure to 20 atm CO_2 at room temperature for several days and finally compression moulded into a plug using a hand operated arbor press. The density of the compacted plug was 1.0 g cm^{-1}. The plug, weighing about 440 mg, was placed directly on the Ni-Cr macrosample holder of a Mettler Thermoanalyzer-1 and degassed at 35°C to $<10^{-5}$ torr for 24 h. Sorption isotherms for CO_2 (Matheson, bone dry) were determined gravimetrically. With the addition of each aliquot of gas the sample weight increased rapidly during the first 1–2 min and was assumed to be at equilibrium after 10–15 min. At several points along the isotherm, waiting times of 30–60 min confirmed the assumption of equilibration at the shorter times.

Sorption isotherms were measured at 35, 45, 55 and 35°C with at least 24 h at a pressure of $<10^{-5}$ torr allowed for degassing the sample between measurements.

RESULTS

Sorption isotherms for CO_2 in PET over the pressure range of 25–760 torr are shown in *Figure 1*. The sorption capacity for CO_2 in this sample of PET at 1 atm and 35°C is 2.5 cc(STP)/cc(polymer); this is about 1.5 times greater than found for the sample studied by Koros *et al.*[4] This is consistent with the fact that the present sample is 66% amorphous compared to the ~40% amorphous content of the biaxially oriented sample used by Koros. Michaels, Vieth and Barrie[5] reported a sorption capacity for CO_2 of 1.5 cm^3(STP)/cm^3(polymer) at 1 atm and 25°C for a sample of PET which was 57% amorphous. Unfortunately, we do not know the thermal history of the sample used by Michaels *et al.*, or whether the sample was conditioned by exposure to high pressure CO_2 before the sorption measurements. Koros has suggested that the

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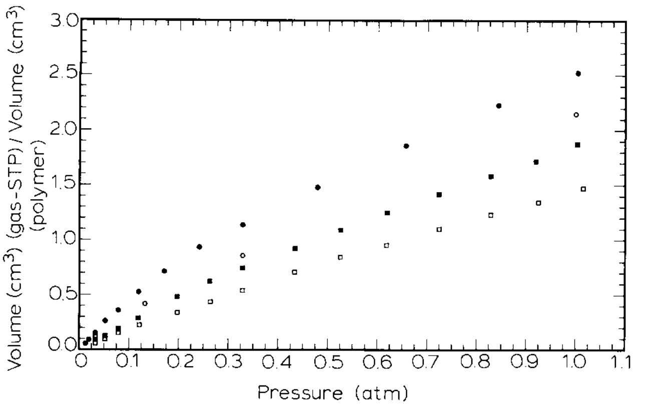

Figure 1 Gravimetric sorption isotherms for CO_2 in PET (66% amorphous). $T=35°$ (●); 45° (■); 55° (□) and 35°(○)

solubility coefficient for CO_2 in PET at 20 atm could be as much as 30% lower in an unconditioned film than in a conditioned one[6]. At lower pressures the difference may be even greater.

The effect of sample thermal history is clearly shown in *Figure 1*. The sorption capacity for CO_2 at 35°C and 1 atm is about 15% lower after measurement of the 55°C sorption isotherm than for the virgin sample.

The isosteric heat of sorption can be calculated from

$$\Delta H_{\mathrm{I}} = zR[\delta \ln(p)/\delta(1/T)]_C \qquad (1)$$

where z is the compressibility factor for CO_2 and R is the gas constant. Since the experimental sorption isotherm data was obtained with the pressure p as the independent variable it is necessary to find a suitable method for determining the sorption isosteres (p vs. $1/T$ at constant C) which must be used with equation (1). In order to avoid biasing the analysis towards a particular model of sorption we choose to use a linear interpolation of the experimental data to develop the p vs. $1/T$ isosteres. Since the isotherms are highly curved, the method of linear extrapolation works best when the experimental points are closely spaced as in *Figure 1*. An alternative method of interpolation, useful when the experimental points are not closely spaced is to account for the curvature of the sorption isotherm with a polynomial. We find that a third-order polynomial in concentration of the form

$$p = \mathrm{a}C + \mathrm{b}C^2 + \mathrm{c}C^3 \qquad (2)$$

where a, b and c are constants, fits the sorption isotherms well. No matter which method is used to determine the isosteres one should use caution in extrapolating far outside the data set.

The isosteric heat of sorption at 45°C, calculated from sorption data obtained at 35 and 55°C, is shown in *Figure 2*. The change in z over the pressure range examined here was negligible[7] ($<2\%$) so z was assumed to be equal to 1 in equation (1). The values of p were calculated by straight-line interpolation and limited to the range in C which was common to both data sets. Thus, the isosteric heat of sorption was determined over a range from the lowest gas concentration measured at 35°C (0.5 cm^3(STP)/cm^3(polymer) to the highest sorption value measured at 55°C (1.5 cm(STP)/cm^3(polymer). This procedure avoids introducing uncertainty due to extrapolating the sorption isotherms. The isosteric heat of sorption calculated in this way varies from about -10 kcal mole^{-1} when $C = 0.5$ cm^3(STP)/cm^3(polymer) to about -8 kcal mole^{-1} when $C = 1.5$ cm^3(STP)/cm^3(polymer). For the data of *Figure 2*, the isosteric heat calculated by the polynomial interpolation method is similar to but smoother than that calculated using the straight-line interpolation method.

Since it is certain that thermal cycling alters the sorption capacity of glassy polymers, calculated isosteric heats of sorption can have no simple interpretation as they might have for rigid glasses or inorganic solids. In the present example, the magnitude of the ΔH_{I} depends on the order in which the sorption measurements were made; using data from the sorption measurement at 35°C made subsequent to the measurement at 55°C gives a ΔH_{I} that is about 3 kcal mole^{-1} more positive than that shown in *Figure 2*. No matter which way one chooses to calculate the isosteric heat of sorption in this PET–CO_2 system, ΔH_{I} becomes more positive with increasing gas concentration in the range of 0.5–1.5 cm^3(STP)/cm^3(polymer).

DISCUSSION

As with all sorption studies we must be confident that the sample is representative of the bulk material. We used a powdered sample in order to facilitate sorption equilibrium in a reasonable time period. The moderate surface area (7.5 m^2/g) could provide additional adsorption not found in bulk polymers. However, the sorption capacity at 1 atm for our powdered sample at 35 and 55°C is ≈ 1.45 and 1.43 times greater than for the sample used by Koros *et al*., while having 1.65 times as large an amorphous fraction. While we cannot exclude the possibility of some surface adsorption, it apparently does not contribute significantly to the total sorption capacity. Use of the powdered sample achieved our goal of rapid equilibration

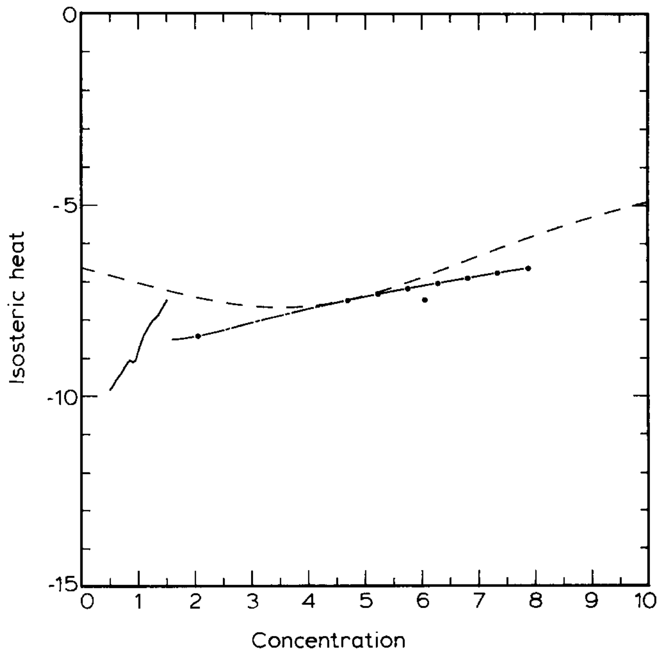

Figure 2 Calculated isosteric heat of sorption in kcal mol^{-1} for CO_2 in PET at 45°C calculated from low pressure sorption data and using equation (1). (———): calculated from high pressure sorption data (ref. 4) using equation (1); (–·–·–): high pressure sorption data using equation (5), (– – –). The units of concentration are cm^3(gas-STP)/cm^3(polymer)

to change in pressure. The fact that the powder was compacted to a mechanically stable pellet does not affect gas transport to the interior of the sample since the density of the pellet was still only about 3/4 that of the amorphous polymer.

The observation of nonlinear sorption isotherms for gases in glassy polymers has suggested the possibility that the gas sorption process is the sum of two familiar processes; Henry's law dissolution, typical of gas solution in liquids, and Langmuir-type sorption, typical of gas sorption on solid surfaces[5,8]. The former is proportional to pressure and is suggested to give the nearly linear portion of the isotherm at high pressures. The latter is highly pressure dependent and is presumed to account for the rapidly decreasing solubility coefficient as the gas pressure rises through the first few atmospheres. A simple empirical formalism, known as the dual-sorption mobility model has been developed in order to characterize sorption and diffusion in glassy polymers as the sum of these two mechanisms[9]. In the dual-mode formalism the sorption capacity of a glassy polymer is expressed as the sum of the concentration of gas dissolved by ordinary dissolution C_D, and concentration of Langmuir sorbed gas C_H,

$$C = C_D + C_H \tag{3}$$

$$C = k_D p + \frac{C'_H bp}{(1+bp)} \tag{4}$$

where k_D is the Henry's law constant, C'_H is the Langmuir saturation capacity, and b is the Langmuir affinity coefficient. Koros *et al.* showed that when the sorption capacity is represented in terms of the dual-mode model then the isosteric heat of sorption is given by[1],

$$\Delta H_l = zR \frac{k_D \Delta H_D + \dfrac{C'_H b(\Delta H^* + \Delta H_b)}{(1+bp)} - \dfrac{C'_H b^2 \Delta H_b p}{(1+bp)^2}}{k_D + \dfrac{C'_H b}{(1+bp)} - \dfrac{C'_H b^2 p}{(1+bp)^2}} \tag{5}$$

where ΔH_D, ΔH_b and ΔH^* are the apparent enthalpies derived from van't Hoff plots of the Henry's law coefficients, the Langmuir affinity coefficients, and the Langmuir saturation capacities, respectively. Based on the dual-mode analysis of the high pressure CO_2–PET sorption data, Koros *et al.* showed that ΔH_D and ΔH_b were reasonably independent of temperature but that the van't Hoff plot of C'_H was curved and therefore probably did not have a simple physical meaning.

According to the dual-mode analysis, a minimum in the ΔH_l vs. concentration curve can arise because the molecules assigned to the Langmuir fraction are more energetic than the dissolved molecules but account for a decreasing fraction of the population as the gas concentration increases. The minimum occurs when the concentration is near the value of C'_H. At higher temperatures the value of C'_H decreases[9,10] so the minimum would appear at lower concentration.

The predicted minimum in the isosteric heat of sorption is not observed in the experimental ΔH_l calculated from data (shown in *Figure 1*) on the low pressure sorption of CO_2 on PET. The same conclusion is reached from an analysis of the low pressure sorption data of Michaels *et al.*[5] They reported low pressure sorption isotherms for CO_2 in an amorphous PET sample at 25 and 40°C and a high pressure isotherm at 25°C. From analysis of the high pressure data, Michaels *et al.* reported a value of 4.25 cm^3(STP)/cm^3(polymer) for C'_H so one would expect the minimum in the ΔH_l vs. concentration curve for their sample to appear at a concentration somewhat lower than this. We have used the straightline interpolation method to calculate ΔH_l from their low-pressure experimental data. Equation (1) yields values for the isosteric heat of sorption which increase from -8.6 kcal $mole^{-1}$ at a concentration of 0.5 cm^3(STP)/cm^3(polymer) to about -7.3 at 1.25 cm^3(STP)/cm^3(polymer). Again, there is no indication of a minimum in the ΔH_l curve.

The isosteric heat of sorption for CO_2 in PET at 45°C reported by Koros[11] is reproduced in *Figure 2*. Koros calculated this curve from equation (5) using coefficients determined by the dual-mode analysis of his high pressure sorption data[4]. In *Figure 2*, the ΔH_l curve based on the dual-mode analysis becomes more negative until a shallow minimum is reached at a concentration of about 4 cm^3(STP)/cm^3(polymer) and then becomes more positive.

Because the history and properties of our sample are different from the properties of the samples used by Koros[4] and Michaels[5] there is no reason to expect the ΔH_l values for these samples to be quantitatively similar. Nevertheless, ΔH_l values for our sample and the Michaels sample become more positive with increasing concentration, opposite the low concentration behaviour reported by Koros (see *Figure 2*). The sorption data from our work and that of Michaels were sufficiently closely spaced that a straight-line interpolation gives a nearly model independent method of constructing the sorption isosteres and determining ΔH_l. We believe that the minimum in ΔH_l curve reported by Koros is an artifact introduced by the use of the dual-mode sorption equation to analyse the data. Below we test this hypothesis by reanalysing the high pressure sorption data for CO_2 in PET using the methods described in the Results section.

The low concentration (pressure) region of the CO_2/PET sorption isotherms contain far too few data points to characterize the curvature of the isotherm well enough to use the straight line interpolation method. Instead, we have fitted the data to a third-order polynomial (equation (2)) and, as above, we have limited the calculation to the interpolated data. There is some tendency for this curve to flatten out at the lowest concentrations. It is impossible to tell if this represents a portending minima in the curve or simply reflects the fact that this highly curved region of the sorption isotherm is grossly under determined for an accurate third-order polynomial fit. From the sorption data at 35 and 55°C we find values for ΔH_l at 45°C which increase from -8.3 kcal $mole^{-1}$ at 1.6 cm^3(STP)/cm^3(polymer) to -6.8 kcal $mole^{-1}$ at 7.6 cm^3(STP)/cm^3(polymer). The values calculated by fitting the sorption data to a polynomial agree with those calculated from equation (5) only in a limited concentration range (see *Figure 2*).

The isosteric heat of sorption measurements presented here suggest that PET has a high affinity for CO_2; ΔH_l ranges from about -10 kcal mol^{-1} at low CO_2 concentrations to around -7 kcal mol^{-1} at moderate concentrations. On the other hand, apparent heats of solution for CO_2 in liquids and rubbers range from -1 to -3 kcal mol^{-1} and in glassy polymers from -4 to

-7 kcal mol^{-1}. We are reminded, however, that apparent heats of solution, determined from the temperature dependence of the gas solubility under *isobaric* conditions, are *not* indicative of the quantity of enthalpy obtained on moving molecules from the gas to the sorbed state, except when the solution obeys Henry's law. The isosteric heat of sorption, on the other hand, corresponds to the differential heat of sorption, a measurable quantity. Thus, apparent heats of solution for liquids and some rubbers do represent the true differential heat of solution, but underestimate the true heat of solutions in glassy polymers whose solubilities show negative deviations from Raoult's law.

Are values of -10 to -7 kcal mol^{-1} for the heat of solution of CO_2 in PET reasonable? There have been no reports of direct calorimetric measurements of differential heats of sorption for gas–polymer systems. Low gas solubilities and relatively slow diffusion challenge the sensitivity of current instrumentation. Some insight to the energetics of sorption can be gained by considering the nature of the interactions between the gas and the polymer. For the sorption of CO_2 in organic materials, the principle contributions to the heat of sorption are the dispersive, repulsive and quadrupole interactions. (We eliminate from consideration those systems where significant contributions from hydrogen bonding or dipole interactions may be involved.) Of these, the dispersive interaction is by far the most important for solutions involving hydrocarbon materials. Dispersive interactions depend on sixth-power of the r.m.s. distance separating the molecules. The partial molar volume of CO_2 in many liquids and rubbers is about 55 cm^3 mol^{-1}. In glassy polymers, whose rigidity tends to resist swelling by penetrants, the partial molar volume of CO_2 may be much smaller. Recent dilation measurements of polycarbonate indicate a partial molar volume of CO_2 of 35 cm^3 mol^{-1} [12]. All other factors being constant, the smaller space occupied by CO_2 in glassy polymers compared to liquids or rubbers implies a factor of three increase in the dispersive interaction energy. This means that we can expect the true heat of solution for CO_2 in glassy polymers to be three times greater than it is in rubbers and hence the values of -7 to -10 kcal mol^{-1} found in this study are reasonable.

We find that the isosteric heat of sorption for CO_2 in PET monotonically increases (becomes more positive) as the gas concentration increases, regardless of which sorption data are used. The reports of the ΔH_1 vs. concentration curve possessing a minimum in PET must be attributed to a bias introduced by fitting the sorption data to the dual-mode equation. This is probably true for other glassy polymer–gas systems which have been analysed by the dual-mode model and show a minimum in the ΔH_1 curve[13–14], although we have not attempted to recalculate ΔH_1 in those systems using the model independent method.

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