Sorption of Methylene Chloride in Polyethylene Terephthalate

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Synopsis

Sorption of methylene chloride in polyethylene terephthalate has been performed at three different temperatures: 21, 34, and 48°C. The solubility data are explained through dual sorption. The diffusivities are more difficult to explain since some anomalous effects were present.

INTRODUCTION

A number of recent publications have reported the results of sorption experiments on vapors in poly(ethylene terephthalate) (PET). Patton et al.[1] have reported data in benzene-amorphous PET system. The diffusion was seen to be classical but the solubilities were shown to exhibit the dual sorption character. Makarewicz and Wilkes[2] also studied a number of vapors including methylene chloride in amorphous PET and showed that whereas diffusion was classical, crystallization was induced. The activities were not measured but were estimated to be high. The experiments were confined to one temperature. Similar results were also reported by Durning and Rebenfeld[3] and Durning et al.[4] over a wider range of temperatures but with activities very close to one. In semicrystalline PET, Haga[5] reported that methylene chloride and similar chlorinated hydrocarbons, exhibited anomalous diffusion, that is, the fractional mass uptake M_t/M_∞ varied as t^n, where $n = 1/2$ in the classical case and $n = 1$ in case II: Haga's data had values of n between 1/2 and 1.

In effect, whereas strongly interactive systems such as methylene chloride and PET, show a variety of behaviors, very little appears to be known in such systems regarding diffusivities and solubilities. Described below are the experiments and results of sorption of methylene chloride vapors at moderate activities in PET.

EXPERIMENTAL

Apparatus

The experimental setup was standard. Methylene chloride was flashed and vaporized into a 13 liter flask which was then isolated. The vapor was fed to an electrobalance which was previously evacuated through a trap. The evacuation was monitored with a MacLeod gage. Durning the experiment the temperature and pressure were continuously monitored inside the electrobalance. A few results were rejected because these values changed. The pressure was recorded with a pressure gauge which read to a torr and the temperature

with a digital thermometer with $\pm 0.2^\circ$C accuracy. High vacuum valves were used. The vapor source and the electrobalance were encased in an air bath with a heater, muffle fan, and a temperature controller of $\pm 0.2^\circ$C with its sensor strapped to the exterior of the hangdown tube of the electrobalance. The assembly was placed on a table top separated from the stand by rubber pads. The feed to the vapor source, the trap, and the vacuum pump had separate supports.

Materials

Methylene chloride was analytic grade. Glassy amorphous PET films of 2 mil thickness, supplied by Eastman Kodak, were used. PET has a glass transition temperature of about 70°C, but no checks were made. No obvious impurities were found in infrared spectroscopy. Sample sizes were typically of the order of 40–80 mg. The films had been stored away from light for about a year.

Both differential and integral sorption runs were performed though mainly the former have been reported. Differential sorption gives diffusivities as functions of concentration. However, it is possible that such systems being always nearly equilibriated anomalous effects may be excluded. Consequently, at a fixed temperature, a full set of differential sorption tests were made on the same sample by increasing the pressure in steps. When the maximum was reached it was desorbed to vacuum. The desorption curve (plotted as fraction desorbed) was always found to lie between the two extremes of fractional uptake curves of sorption. All responses were found to be classical. In addition, fresh samples were used to check responses under integral sorption where the final pressures were chosen at random. These two showed only classical sorption.

RESULTS

The solubilities have been shown in Figure 1. Regression using the dual sorption model

$$C = K_D P + \frac{C_H' b P}{1 + bP} \tag{1}$$

gave parameters which have been plotted in Figures 2 and 3. In Figure 2 it has been shown that K_D and b satisfy Arrhenius relationship with temperature. It is more difficult to correlate C_H'. In Figure 3 the simplest possible correlation is sought for C_H' as a function of temperature. It is seen there that $C_H' = 0$ at a temperature of about 65°C. Since the dual sorption mode should vanish at the glass transition temperature T_g, one may then assume $T_g \approx 65^\circ$C here which is a reasonable value for PET. The data obtained here for methylene chloride, those of Patton et al.[2] for benzene and of Yasuda et al.[6] for water (all in amorphous PET) fail to correlate against reduced temperature, in contrast to those for ethyl cellulose.[7]

A set of differential sorption curves at 34°C is shown in Figure 4. The fact that the responses at large activities lag behind relative to $t^{1/2}$ can be clearly seen. Makarewicz and Wilkes[2] have shown that at large activities the vapor
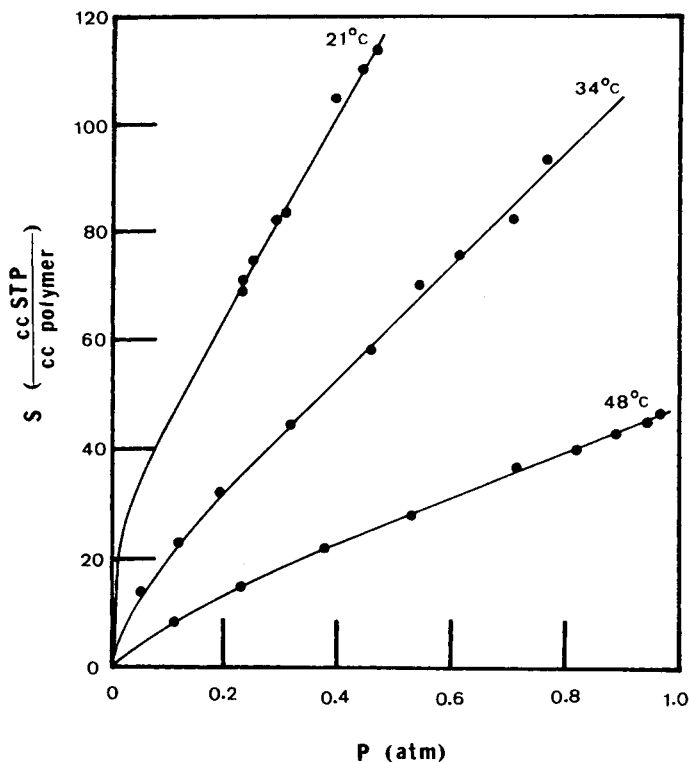
Fig. 1. Solubility of methylene chloride in PET.

diffuses inside the polymer with a sharp front. The rate of movement of the front is proportional to $t^{1/2}$ except at short times when it lags behind. If the region behind the front is nearly saturated then the fractional mass uptake would increase at a rate proportional to the rate of movement of the front, that is, lag behind the $t^{1/2}$ response as seen in Figure 4. In terms of anomalous response discussed earlier the fractional mass uptake correlates first as t^n with n greater than 1/2 and later as $n = 1/2$. The half-times have been used to obtain mutual diffusion coefficients and have been plotted against activity in Figure 5. The curve at 21°C represents integral sorption and the corresponding activities the stepped up values. The results from the anomalous sorption clearly fail to correlate with the cases where sorption is classical. In Figure 5 diffusivities calculated from one set data each from Makarewicz and Wilkes[2] and Durning and Rebenfeld[3] for activity very close to one have been plotted as well. The values are close to values reported here. It is noteworthy that in these cases crystallization takes place and probably some condensation on the samples occurs since the vapors were close to saturation.

According to Fujita[8] the thermodynamic diffusivities D_T are related to mutual diffusivities D by

$$D_T = \frac{D}{1 - v_1}\left(\frac{\partial \ln c}{\partial \ln a}\right)_T \qquad (2)$$
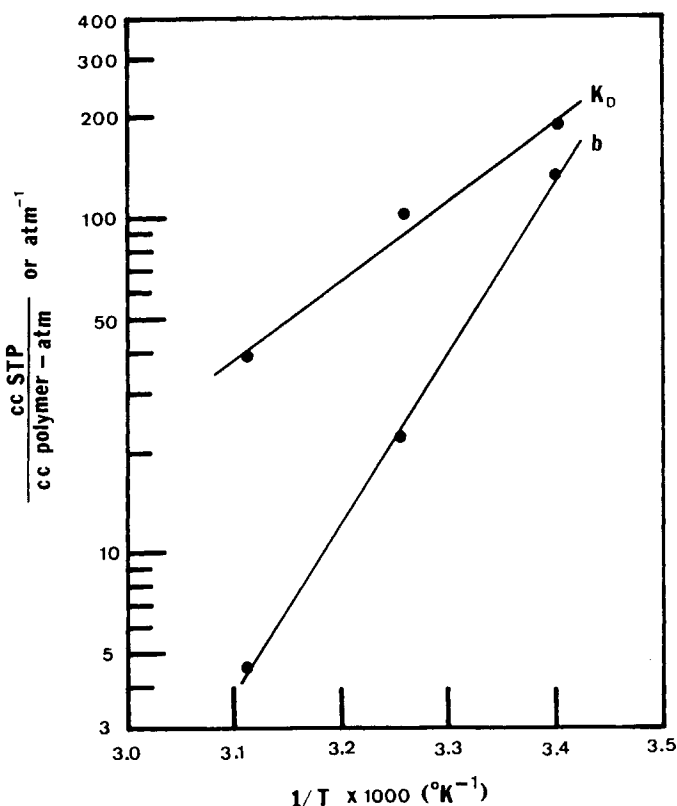
Fig. 2.   Arrhenius plots of K_D and b, see Eq. (1).

where a is the activity, c the concentration, and T is the temperature. Further, the term $1 - v_1$ on the right hand side has been used to correct for swelling in some form. According to Fujita[8]

$$D_T = RTA_d \exp\left[-\frac{B_d}{f + \beta v_1} \right] \tag{3}$$

where R is the gas constant, A_d is a constant, B_d, f, and β are functions of temperature only. Using Eqs. (2) and (3), and data from Figures 1 and 5, and density of PET of 1.336 g/cm^3, and density of methylene chloride as that of the saturated liquid, D_T values were obtained and plotted as $[\ln(D_T/D_o)]^{-1}$ versus $1/v_1$ in Figure 6. Here D_o is D_T at infinite dilution. According to Eq. (3) the plots should be linear. Curvatures are observed at large values of v_1. That deviations from Fujita's relation should be observed at large concentrations is reasonable in view of more sophisticated theories.[9]

Infrared (IR) spectroscopy,[10] small and large angle x-ray diffraction were used to detect morphological changes caused by vapors at moderate to large activities. No significant or reproducible changes were detected. (In contrast these PET films when soaked in liquid methylene chloride showed distinct lamellar spacings.) Consequently we conclude that there was at least no
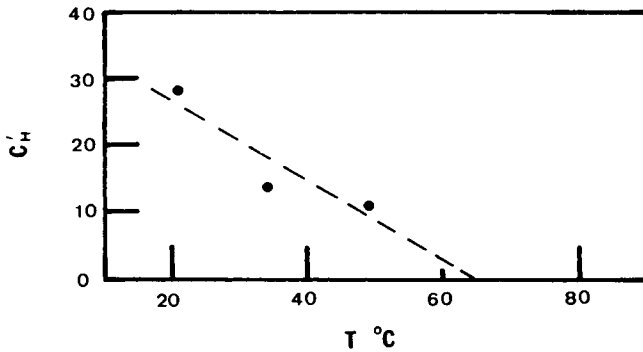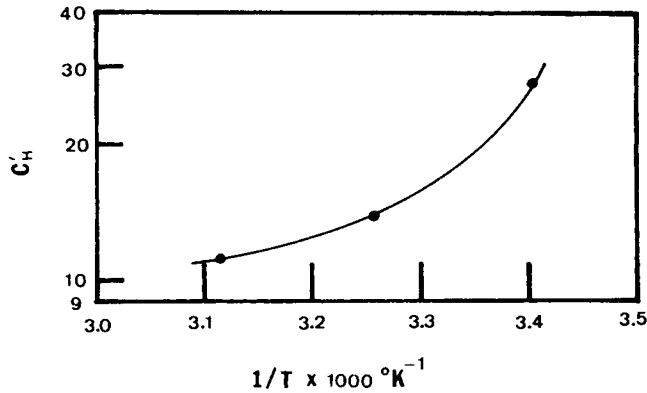
Fig. 3. An apparent correlation for C'_H showing the point where it vanishes.

obvious indication that crystallization took place in methylene chloride vapor. However, it is known that crystallization will take place only above the glass transition temperature T_g. By using Kelley-Bueche equation and the parameters given in Refs. 11 and 12, the volume fractions of methylene chloride needed to depress T_g to room temperatures can be shown to be very low. To resolve this contradiction one should both check the morphological changes and estimate the depression in T_g more accurately beyond the conventional practices.

CONCLUSIONS

Whereas the data obtained here conform to the behaviors suggested for glassy amorphous polymers and for PET in particular, more work would be required in future to achieve generalizations in strongly interactive systems.
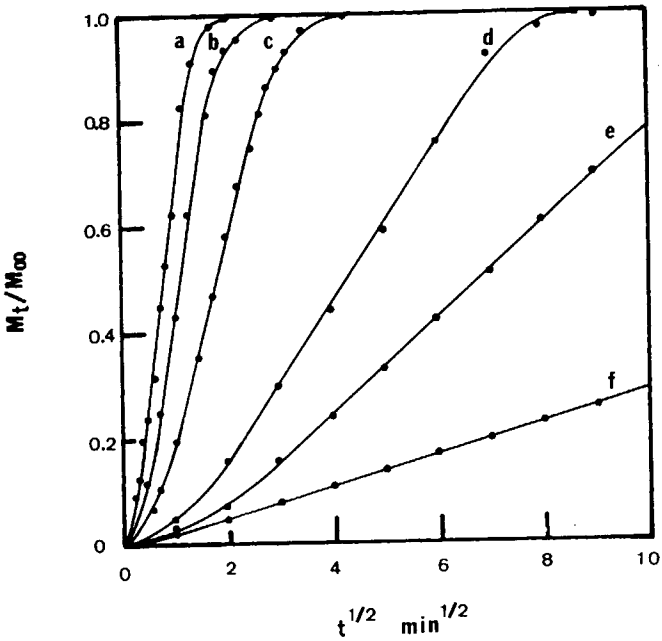
Fig. 4. Sorption responses at 34°C: (a) 540–583 mm; (b) 413–468 mm; (c) 350–413 mm; (d) 244–350 mm; (e) 150–244 mm; and (f) 94–150 mm of mercury.
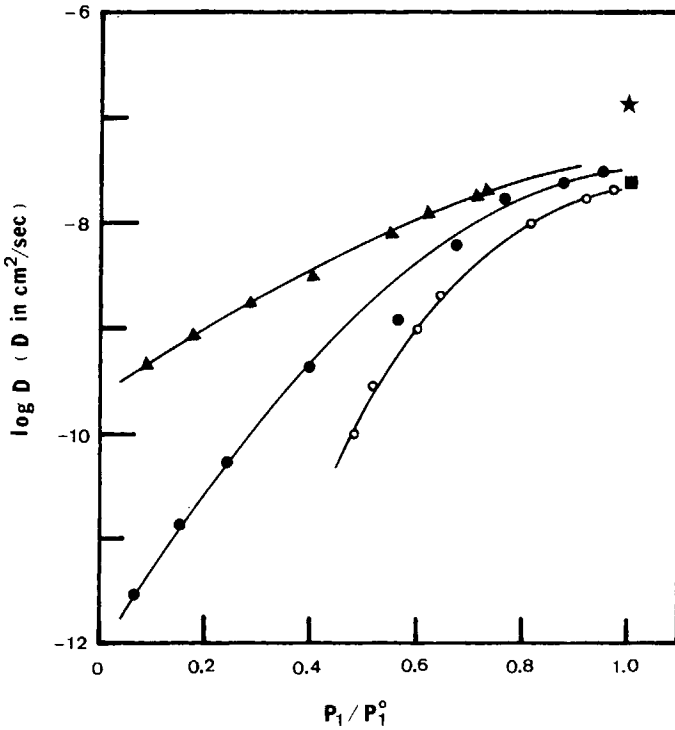

Fig. 5. Diffusivities as function of vapor activity. The curve at 21°C is integral response as are the points from other works indicated, which are: (■) Ref. 2 (24°C); (∗) Ref. 3 (38°C). The remaining are from differential response studies: (○) 21°; (●) 34°C; (▲) 48°C.
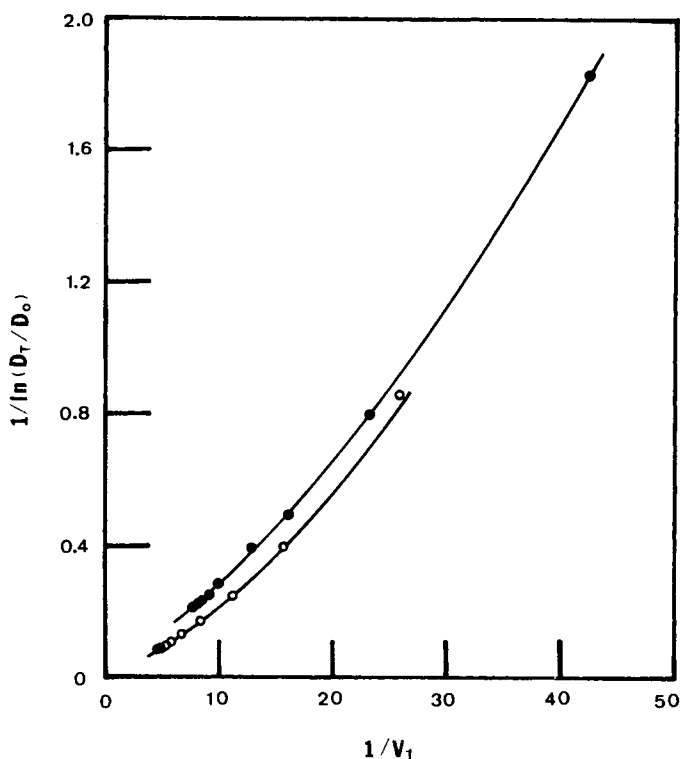
Fig. 6. Thermodynamic diffusivities have been plotted against the penetrant volume fraction using a functional form suggested by Eq. (3): (○) 48°C; (●) 36°C. The theory suggests that straight lines should result.

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