

A Study of the Transport Properties of Acetylene through a Highly Oriented Polyethylene Fiber

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SYNOPSIS

The transport properties of acetylene in a high modulus polyethylene fiber have been studied in detail over the temperature range of 25 to 65°C. Diffusion coefficients for the fiber are about four orders of magnitude lower than values cited for isotropic high density polyethylene. In keeping with this, a much higher apparent activation energy of diffusion (*ca.* 80.64 ± 0.53 kJ mol⁻¹) was found. The solubility of acetylene in the fiber (*ca.* 0.158 cm³ C₂H₂ STP/cm³ PE @ 76 cm Hg), is lower, but of the same order of magnitude as that expected for isotropic polyethylene. The apparent heat of solution was determined, within experimental limits, to be zero. It is concluded that the acetylene is neither chemically nor physically absorbed onto the fiber, but freely diffuses, according to Fick's law, through the amorphous regions of the polymer.

INTRODUCTION

It has been shown recently,¹⁻⁴ that gamma or electron beam irradiation of polyethylene fiber in the presence of acetylene greatly improves the creep behavior. This is associated with the ability of acetylene to accelerate dramatically the process of radiation enhanced crosslinking in polymers.^{2,4,5} In developing a closer understanding of the role of acetylene in this process, it is necessary to know more of the transport properties of the gas in the polymer.

Much work has been done on the diffusion of gases in isotropic polymers.⁶⁻⁸ Because of general interest in high barrier materials and their possible applications in packaging, some research has also been carried out on oriented films with helium and oxygen.⁹⁻¹² However, to date there appears to be no data available for the transport of acetylene or physically and chemically related gases through oriented polymers, particularly in the drawn, filamental state. One reason for this is that it is difficult to measure the transport properties of gases in fine filamental fibers. Unlike film membranes, these fibers do not lend themselves to post diffusion concentra-

tion profile determination by techniques such as mass spectrometry. Similarly, it is not easy to envisage how a Matano method^{13,14} can be used, since gas concentration profiles in fiber filaments are not conveniently obtainable. Therefore, it seemed appropriate to study the transport properties of acetylene in a highly oriented fiber, with a simple but effective system involving external gas concentration monitoring. Although this method does not have the high accuracy that can be obtained with some of the film techniques, it does provide a system in which the temperature can be readily changed in order to study the resulting changes in the transport properties. In polyethylene, when no chemical reactions occur, the changes are known to obey the Arrhenius theory.⁷

EXPERIMENTAL

Materials

Acetylene gas (B.O.C. Ltd., standard grade) was used as purchased, no further purification being required for the purposes of this study. High modulus polyethylene fiber was obtained from SNIA Co., Italy (SNIA HMPE 1800 den, 1728 fil, fil radius = 6.1788×10^{-4} cm, draw ratio *ca.* 30, $M_w = 130,000$, $M_n = 12,000$).

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Method

The system used here is based on a technique previously described by Michaels and Parker,¹⁶ for the measurement of gaseous solubility, but with a diaphragm type digital readout transducer (K.H. Instruments PCO1A) as the pressure gauge. The apparatus is shown schematically in Figure 1. The fiber (ca. 35 g) is wound between flanges on a stainless steel spool, which fits snugly in a stainless steel cylinder. Sufficient fiber is wound to fill the spool and thus to occupy a high proportion of the volume available. The end of the cylinder is closed by a stainless steel plate with a vacuum tight 'O' ring seal. A side tube provides access for admission and evacuation of gases and is connected to the pressure transducer. The complete constant volume unit is immersed in a water bath (Grant Instruments SE50) at the respective experimental temperature. The water bath and entire system are covered with an insulated box to ensure constant temperature conditions. The cylinder is connected, through suitable valves and couplings, either to a high speed, two stage rotary vacuum pump (Edwards E2M-12) or to a source of acetylene gas.

In the experiments, the equipment was initially evacuated overnight to remove all gases from the fibers and the surrounding walls of the apparatus. The pressure was monitored with the pressure gauge. Acetylene was then admitted from a preheated glass flask, which was submerged in the water bath at the same temperature and at approximately one atmosphere pressure. After the required initial gas pressure was achieved, gas admission from the flask to the cylinder working volume was shut off. Pressure fall measurements, due to sorption in the working

volume, were taken at convenient intervals of time, depending on the temperature under investigation, until equilibrium was reached. Following equilibrium, the apparatus was evacuated for about 30 sec. This period of time was required to remove all free undissolved gas from the system. Pressure rise measurements, due to desorption, were then taken at convenient intervals of time as for sorption, until equilibrium was again reached. In practice, both sorption and desorption were allowed to continue until an apparent relatively constant gradient was achieved. This gradient is attributed to small amounts of sorption and desorption on the walls of the surrounding apparatus. From this gradient the true sorption and desorption profiles of acetylene through the fiber were extrapolated. This procedure was adopted because it was found to be almost impossible to reproduce an exact pressure, in order to mimic a blank run, without fiber. This procedure also saved on changeover time and avoided the necessity of recalibration of the apparatus.

The solubility of the acetylene in the yarn is determined from the change in the "equilibrium" pressure levels observed when the content of gas in the polymer readjusts to a change in the pressure of the surrounding gas. The specific solubility constant, S (cm^3 gas (STP)/ cm^3 fiber @ 76 cm Hg), for the gas in the polymer has been shown¹⁵ to be given by the following equation:

$$S = \frac{V_{gs} P_{fe} - P_s \cdot T_o}{V_y P_{ie} - P_{fe} T} \quad (1)$$

where V_{gs} , V_y are the free gas space volume and the yarn volume, respectively. P_{ie} is the initial equilib-

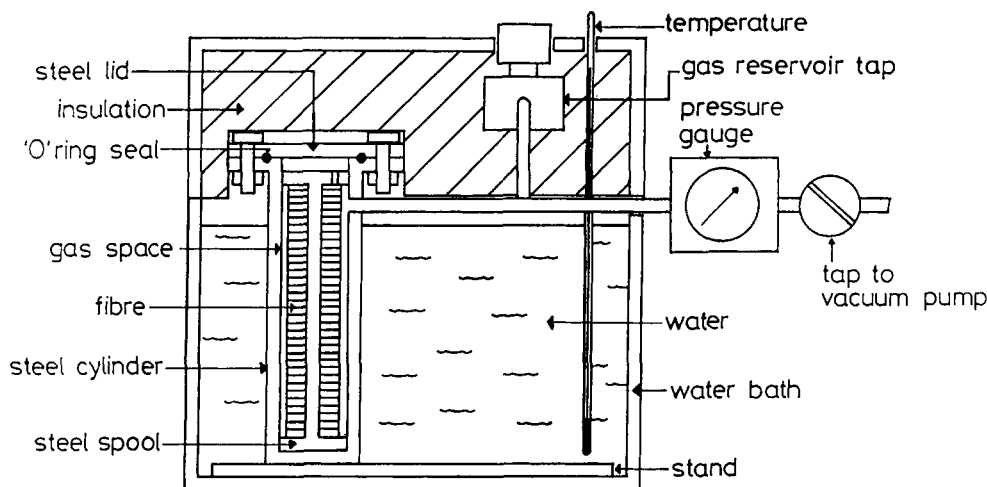


Figure 1 Schematic diagram of sorption/desorption apparatus.

rium pressure before outgassing free undissolved gas, P_s and P_{fe} are the start pressure after out-gassing and the final equilibrium pressure, respectively, and T_o and T are the reference temperature (273.15 K) and the temperature of the measurement respectively, both expressed in K.

The volume of the apparatus was precalibrated by admitting air at atmospheric pressure from the temperature stabilizing flask into the steel cylinder, which was under vacuum. The procedure was carried out a number of times both with and without fiber. Volumes were calculated from the drop in pressure corresponding to the concomitant increase in volume of the system. Prior to collecting acetylene diffusion data for the purposes of this study, the method was checked with oxygen. The resulting values compared very well with those obtained from a study¹² of oxygen diffusion in highly oriented polyethylene films of various draw ratios up to 22 times.

The diffusion coefficient was obtained from the variation in the pressure in the container with time. The yarn can be considered as an assembly of infinitely long cylinders. After these cylinders have been saturated with acetylene and the surplus acetylene has been pumped away, the rate of pressure rise in the sealed container was determined by the diffusion coefficient. It can be shown, based on work by Crank,¹⁵ that after time t from the start of the desorption process, the concentration, and hence the pressure of the gas in the container, will be given by:

$$\ln(1 - Z) = -\frac{B^2}{r^2} \times D \times t + \ln \frac{4}{B^2} \quad (2)$$

where r is the cylinder (filament) radius, D is the diffusion coefficient, B is the zero order Bessel function for infinitely long times ($= 2.405$), and Z is the relative desorption given by the ratio of the change in the gas concentration after time t to the total change required to reach equilibrium.

$$\text{Thus, } Z = \frac{c_t - c_i}{c_e - c_i} = \frac{p_t - p_i}{p_e - p_i}$$

where the c and p refer to the concentration and the pressure, respectively, of the gas at the cylinder surfaces, with the subscripts i , t , e corresponding to the initial state, the value at time t , and the final equilibrium value, respectively.

A plot of $\ln(1 - Z)$ against time thus shows a straight line with slope

$$-\frac{B^2}{r^2} \times D$$

from which D can be obtained. Equation (2) is strictly valid only where the surface concentration remains constant, but variations during the desorption process are expected to be small and to result in, at most, an error of 5%.

Although a similar expression can be developed for the sorption mode, it was found that temperature effects introduced by the gas flow caused uncertainties in the initial pressure readings. The effect is minimal at room temperature, but increases as the temperature is raised and, hence, since the resulting diffusion coefficients become unreliable, these values have not been included.

RESULTS AND DISCUSSION

Specific Solubility

The specific solubility constant (S) was determined at temperatures ranging from 24.5°C to 65°C and within experimental error remains constant within those limits (Table I). Since the desorption rate increases with temperature, the value obtained at 65°C may suffer a small loss of gas as the free gas is extracted and, hence, be slightly low. Disregarding this value gives a mean value for S of 0.158 cm³ C₂H₂ (STP)/cm³ P.E. @ 76 cm Hg with a standard deviation of 0.010. Since diffusion takes place through only the amorphous regions of the polymer, the value for a completely amorphous polymer will be higher. The crystalline volume fraction v_c , of the SNIA fibers, as derived from the density, is 0.7586 ($v_c = (\rho \text{ fiber} - \rho \text{ amorphous}) / (\rho \text{ crystalline} - \rho \text{ amorphous})$ with $\rho \text{ fiber} = 0.965$, $\rho \text{ crystalline} = 1.000$, and $\rho \text{ amorphous} = 0.855$).¹¹

With the acetylene physically excluded from the

Table I

| Temperature (C) | Diffusion Coefficients (cm ² s ⁻¹) | Specific Solubility (cm ³ C ₂ H ₂ STP/cm ³ PE) |
|-----------------|---|--|
| 24.5 | 7.54 × 10 ⁻¹³ | 0.156 |
| 34.5 | 9.63 × 10 ⁻¹³ | 0.165 |
| 44.5 | 6.45 × 10 ⁻¹² | 0.142 |
| 55.0 | 6.20 × 10 ⁻¹² | 0.157 |
| 60.0 | 9.65 × 10 ⁻¹² | 0.172 |
| 65.0 | 6.59 × 10 ⁻¹¹ | 0.127 |

crystalline regions,¹⁶⁻¹⁹ the specific amorphous solubility constant, S_a , will be given by

$$S_a = S/(1 - v_c)$$

and for the above, the figures are $0.656 \text{ cm}^3 \text{ C}_2\text{H}_2 \text{ (STP)/cm}^3 \text{ amorphous P.E. @ 76 cm Hg}$, with a standard deviation of 0.041. This may be compared with a value of $1.048 \text{ cm}^3 \text{ C}_2\text{H}_2 \text{ (STP)/cm}^3$ of completely amorphous polyethylene, derived from work by Michaels and Bixler,⁶ and involving measurements by Van Amerongen²² on the specific solubility of acetylene in natural rubber. This comparison suggests that the high modulus SNIA yarns have a significantly different structure from either the isotropic polymer or from the drawn films previously examined. It is possible that this arises either from a high molecular orientation in the amorphous regions, or it is caused by the presence of intercrystalline bridges, which prevent the acetylene molecules from diffusing into some regions of the polymer. The experimental specific amorphous solubility for the SNIA HMPE fiber yields a ratio of gas molecules to amorphous polyethylene number average molecular weight molecules of 0.41.

The solubility of the acetylene in the amorphous regions of the polymer is also related to the Lennard-Jones force constant (ϵ/K) of the gas by the expression⁶:

$$\epsilon/K = [\ln(S_a) + 5.07]/0.22$$

The Lennard-Jones potentials can be obtained from the second virial coefficients (B) by the method of Hirschfelder et al.²³ Thus, at the critical temperatures $T_c = 308.23 \text{ K}$, $\epsilon_c/K = T_c/1.3$, $B_c = -0.1383$, and at the desired temperature, for example, 20°C ($T_{20} = 293.15 \text{ K}$), $B_{20} = -0.158$, hence

$$\epsilon_{20}/K = \epsilon_c/K \cdot \frac{B_c}{B_{20}} \cdot \frac{T_{20}}{T_c} = 197.4 \text{ K} \quad (3)$$

This gives a value for S_a of *ca.* $0.4833 \text{ cm}^3 \text{ C}_2\text{H}_2 \text{ (STP)/cm}^3 \text{ amorphous P.E. @ 76 cm Hg}$ and, hence, is lower than that derived from the Michaels and Bixler work given above. The corresponding value for S would be $0.1167 \text{ cm}^3 \text{ C}_2\text{H}_2 \text{ (STP)/cm}^3 \text{ P.E.}$ The measurements on the highly oriented SNIA yarns are therefore in better agreement with the theoretical value than those on the amorphous un-oriented material.

Diffusion Coefficients

The variation with time of the pressure in the sealed container for the sorption of acetylene onto the SNIA HMPE fiber at 24.5°C and 1.0368 bar pressure is shown in Figure 2, after the extrapolated correction for sorption into the surrounding apparatus. Figure 3 shows the desorption process at the same temperature, and is almost a mirror image of Figure 2.

The plot of $\ln(1 - Z)$ against time for the desorption process is shown in Figure 4 and, as ex-

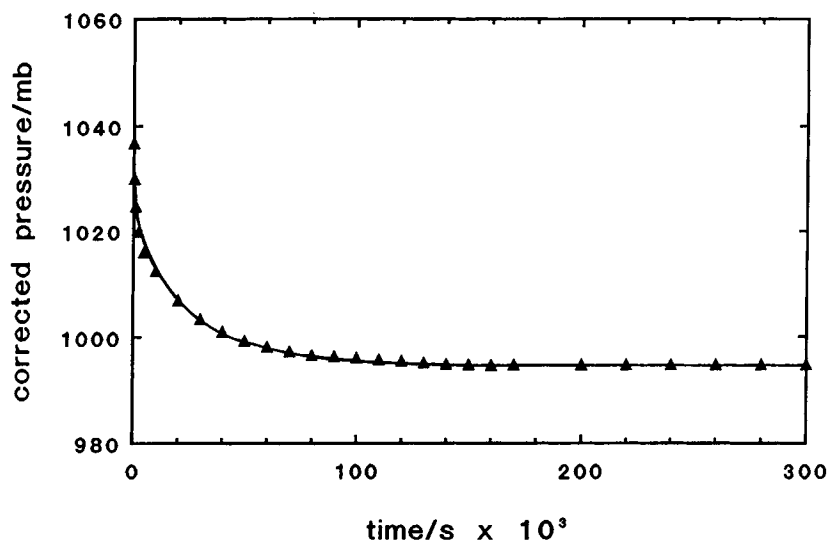


Figure 2 Variation of corrected gas pressure with time to show acetylene absorption by the fibers.

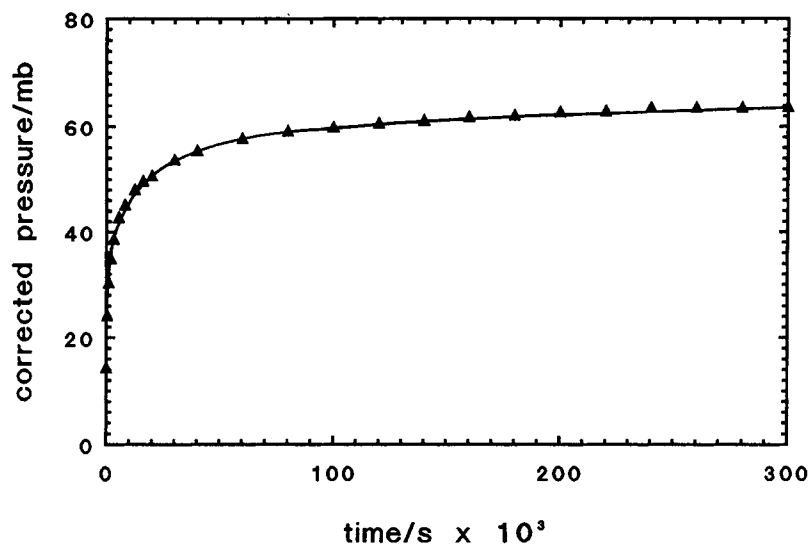


Figure 3 Variation of corrected gas pressure with time to show acetylene desorption from the fibers.

pected, gives a linear relationship from which D can be obtained. The value found is $7.54 \times 10^{-13} \text{ cm}^2 \text{ sec}^{-1}$. At this temperature, mole for mole, within experimental limits, the quantity of acetylene taken up by the fiber was equal to that released on desorption.

From measurements with an extensive series of gases of the diffusion through various undrawn polyethylenes and through natural rubber, Michaels

and Bixler⁷ developed an empirical relationship between the diffusion coefficient, D^* , for completely amorphous polyethylene, the gas molecular diameter, d_c , and the reduced molecular diameter, d_r , allowing for the separation of the CH_2 groupings in the polymer. This relationship gives

$$D^* = (d_c)^2 \exp(3.66 - 1.32d_r) \times 10^{-7} \quad (4)$$

and for acetylene with $d_c = 4.8 \text{ \AA}$ and $d_r = 3.9 \text{ \AA}$ gives a value for D^* of $5.20 \times 10^{-7} \text{ cm}^2 \text{ sec}^{-1}$.

In addition, structural effects caused by crystallinity have been considered by Michaels and Parker⁸ by introducing a "geometric impedance factor," τ , and a chain immobilization factor, β , such that

$$D = D^*/\tau\beta.$$

Thus larger gas molecules will follow a more tortuous path (higher τ) where the chains are tightly bound (higher β) in the proximity of crystalline regions. Work by Michaels et al. indicates a value for τ , based on the crystalline volume fraction of about 0.76, of 5.8, and a value of β , based on the reduced molecular diameter, of 3.5. The value of D is thus $2.56 \times 10^{-8} \text{ cm}^2 \text{ sec}^{-1}$ and is close to that of allene ($D = 25 \times 10^{-8} \text{ cm}^2 \text{ sec}^{-1}$),²⁰ which has similar diffusion characteristics in normal undrawn high density polyethylene.⁷ The experimental value observed for the SNIA HMPE fiber above, is about four orders of magnitude smaller than that expected for isotro-

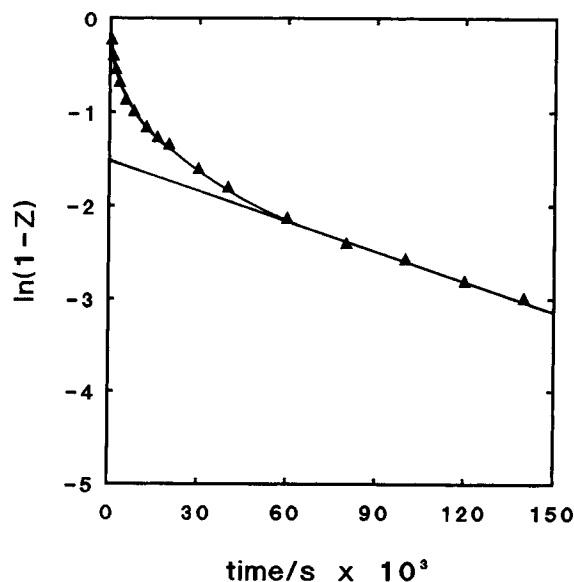


Figure 4 Variation of the relative desorption ratio with time at 297.6 K.

pic undrawn high density polyethylene, whereas the amorphous fraction is almost the same. Holden¹² has shown that the diffusion coefficient for oxygen in highly oriented polyethylene films is about 50 times lower than that of the isotropic feedstock. The highest draw ratio used by Holden was *ca.* 22, and the diffusion coefficient falls by a factor of 10 between draw ratios 11 and 22 in an apparently linear fashion. The lower diffusion coefficients are attributed to higher values for the tortuosity factor, τ , introduced by the orientation. For the larger acetylene molecule, it is therefore reasonable to suppose that the extremely high draw ratio of *ca.* 30 for the SNIA HMPE fiber used here will reduce the diffusion coefficient still further from that observed in undrawn isotropic polyethylene.

Temperature Effects

Similar desorption pressure/time profiles, and $\ln(1 - Z)$ vs. time plots, were obtained at 34.5, 44.5, 55.0, 60.0, and 65.0°C. Since the diffusion coefficients of Fickian diffusion obey Arrhenius temperature dependence, we have

$$\ln D = \ln D_0 - E_D/RT$$

where D_0 is a preexponential constant, R is the gas constant, T is absolute temperature, and E_D is the activation energy of diffusion. A plot of $\ln D$ vs. reciprocal temperature is shown in Figure 5 and from

the slope yields a value for E_D of 80.99 kJ mol⁻¹ with the predicted deviation of slope giving an accuracy range of ± 0.38 kJ mol⁻¹. This can be compared with that obtained by Michaels and Bixler⁷ for isotropic linear polyethylenes from

$$E_D = 2.2(d_r) + 2.6 \text{ k cal mol}^{-1}$$

of 46.78 kJ mol⁻¹ for acetylene, which is close to that for the diffusion wise, characteristically similar molecule allene ($E_D = 47.3$ kJ mol⁻¹).²¹ The larger experimental value encountered in the SNIA HMPE fiber used here, as was suggested for the diffusion coefficient, is most likely an effect of the high degree of macromolecular orientation. Graphical treatment of the Arrhenius equation has increased the accuracy of the extrapolated apparent activation energy of diffusion value and diffusion coefficients from a method, which, for reasons of time, does not lend itself to repeatability error determination.

Since half times ($t_{1/2}$) and equilibrium times (t_e) are functions of the diffusion coefficients, plots of $\ln(t_{1/2})$ and $\ln(t_e)$ vs. reciprocal temperature are the best way to depict the effect of temperature on these parameters. Presented in Figure 6 is such a graph from the desorption data in this study. From it, half times and equilibrium times of sorption can be extrapolated, because true sorption and desorption profiles are almost identical. The graph yields values of $t_{1/2} = 2.67$ h and $t_e = 6.92$ days at 20°C, which are accelerated to $t_{1/2} = 5.02$ min and $t_e = 5.34$ h at 60°C.

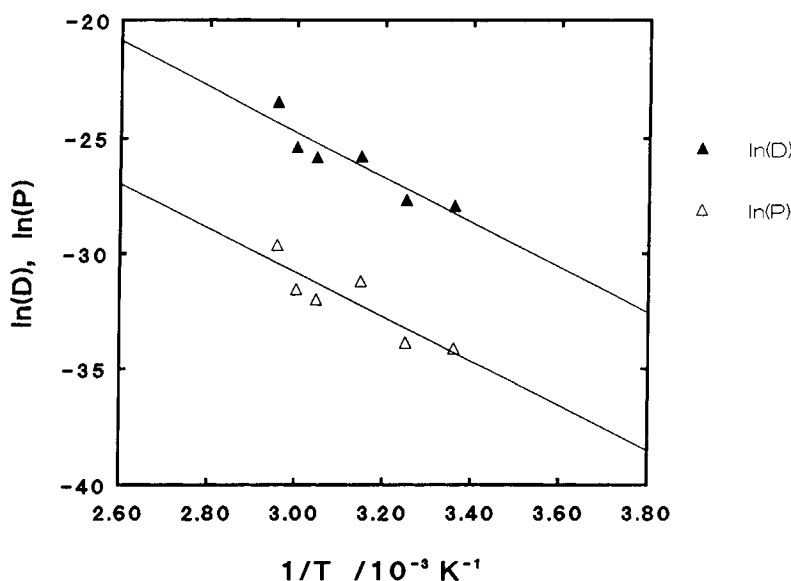


Figure 5 Temperature effects on the diffusion and permeability coefficients.

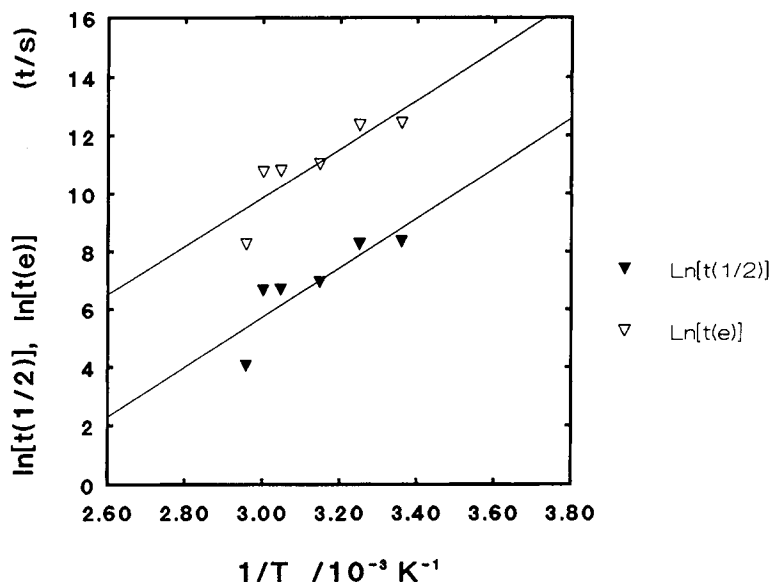


Figure 6 The effect of temperature on the half times and the equilibrium times of the sorption process.

Permeability Coefficients

The permeability coefficient is obtained as the product of the diffusion coefficient and the solubility and at 24.5°C has a value of $1.55 \times 10^{-15} \text{ cm}^3 \text{ (STP) cm cm}^{-2} \text{ sec}^{-1} \text{ (cm Hg)}^{-1}$ and is about four orders of magnitude lower than expected for isotropic polymer. Since the solubility does not vary with temperature, the activation energy for the permeability will be equal to that for diffusion. No data is available for the activation energy of permeability of acetylene in isotropic polyethylene, nor for any method of extrapolating from natural rubber. However, a value of $E_P = 30.54 \text{ kJ mol}^{-1}$ is recorded for the latter method,²² which, as for the expected E_D of acetylene in isotropic polyethylene, may well be much lower primarily for reasons, in this case, of extremely low molecular orientation.

CONCLUSIONS

Diffusion and permeability coefficients for acetylene in highly oriented polyethylene fibers are extremely low in comparison with values expected for normal undrawn high density polyethylene. The apparent activation energies of diffusion and permeability were found to be high, in keeping with a polymer system of high gas barrier properties. These results can be attributed to major changes in polymer structure associated with the very high draw ratio of the fiber.

The solubility of acetylene in the fiber was found to be apparently invariant with temperature, within discernible limits of experimental constraints. It follows that the apparent heat of solution of acetylene in the SNIA HMPE fiber is zero, or indeterminably close to zero, by the technique. Acetylene does not react with the polymer to any significant extent over a period of at least one week. Hence, sorption and desorption are mole for mole reversible Fickian processes and the acetylene is neither chemically nor physically adsorbed onto the polymer fiber, but freely diffuses through the amorphous regions.

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