Solubility and Diffusivity of Bis-(2-Chloroethyl)-Sulfide in Polypropylene

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Synopsis

Solubility and diffusivity have been determined for bis-(2-chloroethyl)sulfide in isotactic polypropylene at temperatures from 15 to 40°C and relative pressures from 0.34 to 1.00. While the solubility in films annealed above 90°C followed the normal variation with the amorphous content, the quenched film had a significantly lower amorphous volume fraction than determined from its density, 46 instead of 60%. The diffusion behavior in the film was found to be invariably Fickian and not dependent on the amorphous volume fraction of the polymer between 0.34 and 0.46. The solubility was found to be independent of the temperature over the range 15–40°C, but dependent on the diffusant concentration. The isotherms were well represented by the Flory-Huggins relation for crosslinked polymers, and values for the interaction constant and the average molecular weight between crystallites have been obtained. The value of the interaction constant, $\mu = 1.13$, is an expression of the low affinity bis-(2-chloroethyl)sulfide has for polypropylene. The intrinsic diffusivity was only weakly dependent on the diffusant concentration. The results were found to be in agreement with Fujita's free-volume theory. The apparent activation energy for the diffusion of bis-(2-chloroethyl)sulfide in isotactic polypropylene was found to be 22.5 kcal/mol.

INTRODUCTION

Absorption and desorption of organic vapors by amorphous polymers are governed by the ordinary Fickian diffusion mechanism when the polymers are well above their glass transition temperature.[1] For such cases the mutual diffusion coefficient may be evaluated from an appropriate analysis of the initial rates of these processes. It is reported that the diffusion coefficient so obtained generally increases exponentially with the diffusant concentration, as also can be predicted from Fujita's free-volume theory.[2]

For semicrystalline polymers, it is well established that the crystalline microstructure plays an important role in determining the permeation properties of the polymer. The crystalline regions are imagined not to dissolve any vapor, to be quite impermeable, and all transport is thought to take place in the amorphous phase. Therefore, a two-phase model[3] of the polymeric matrix consisting of an impermeable phase of crystallites of a certain density randomly dispersed in a conducting amorphous phase has been postulated to explain the solubility data.

The main objects of the present paper were to find how the diffusivity and the solubility of bis-(2-chloroethyl)sulfide are related to the concentration of the diffusant in the polymer in order to establish what kind of limitation is induced on the solution of the diffusion equation.

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THEORETICAL ASPECTS

The distribution of a diffusant in a polymeric film and its change with time during absorption are governed by the one-dimensional differential equation for diffusion due to Fick. The solution to this differential equation depends on the initial and boundary condition taken for the diffusant concentration, as well as on the nature of the mutual diffusion coefficient D. When the diffusion coefficient and the surface concentration are constant, the amount M_t absorbed during time t in a film of thickness l is given by the equation[4]:

$$\frac{M_t}{M_\infty} = 4\left(\frac{Dt}{l^2}\right)^{1/2}\left(\frac{1}{\pi^{1/2}} + 2\sum_{n=0}^{\infty}(-1)^n \text{ ierf } c\,\frac{nl}{2(Dt)^{1/2}}\right) \tag{1}$$

for $c = 0$ at $t = 0$. M_∞ is the amount of diffusant absorbed in the film at equilibrium and ierf c is the inverse complementary error function. The initial slope K of the curve when M_t/M_∞ is plotted against $(t/l^2)^{1/2}$ gives the diffusion coefficient:

$$D = K^2\pi/16 \tag{2}$$

Evidently plots of M_t/M_∞ versus $(t/l^2)^{1/2}$ for a series of samples of different thicknesses should all have the same slope.

It has generally been found that the diffusion coefficient in polymer–organic vapor systems increases with increasing diffusant concentration.[5] Under these conditions the diffusion equation has not been solved analytically. However, the initial slope of the sorption curve yields some mean value of the diffusion coefficient:

$$\overline{D} = \frac{1}{c_0}\int_0^{c_0} D\,dc \tag{3}$$

where c_0 to 0 is the concentration range existing in the film during the absorption experiment.

The sorption method yields a diffusion coefficient that needs to be corrected for the swelling that takes place in the polymer during the absorption of diffusant. If there is no overall volume change on mixing and if one may neglect the intrinsic diffusion coefficient of the polymer in comparison to that of the diffusant, the intrinsic diffusivity can be calculated from the relationship[6]:

$$\mathcal{D} = D(1 - V)^{-3} \tag{4}$$

where V is the volume fraction of diffusant in the amorphous phase of the polymer. Several authors[7-9] have recognized the need to factor the intrinsic diffusion coefficient into two parts, mobility and chemical potential. The self-diffusion coefficient or the thermodynamic diffusion coefficient is related to the intrinsic diffusivity by the relation:

$$\mathcal{D}_T = \mathcal{D}\,\frac{d(\ln V)}{d(\ln a)} \tag{5}$$

where a is a vapor activity of the diffusant.

EXPERIMENTAL

Materials

The polypropylene film was received from Exxon. It had been extruded as a flat film onto a water-cooled chill roll and was more than 96% isotactic. The film density at 25°C, d_{25}, was determined by use of a density-gradient column using p-xylene and chlorobenzene as column liquids as described by Blackadder and Keniry.[10] The original quenched film had a density of 0.889 g cm^{-3} at 25°C.

The amorphous volume fraction α was determined to be 0.603 by using the formula of Vieth and Wuerth[11]:

$$\alpha = (0.936 - d_{25})/0.078 \tag{6}$$

Samples with different crystalline contents were made by annealing the original quenched film for several hours in a vacuum oven, and the final volume fraction of amorphous phase was calculated from the film's density by use of formula (6).

For the sorption experiments, disks of 1.131 cm^2 were cut out of the film and the thickness calculated from the weight and density of the film.

The bis-(2-chloroethyl)sulfide was obtained from the Defence Research Establishment Ottawa and vacuum distilled twice before use. The vapor pressure of the substance in the actual temperature range was calculated from the following expression after Balson et al.[12]:

$$p = 4.825 \times 10^9 \exp(-14528/RT) \tag{7}$$

where p is in Torr and the units of R and T are cal mol^{-1} K^{-1} and K, respectively.

Procedure

The sorption rate and equilibrium concentration of bis-(2-chloroethyl)sulfide in the films were measured with a Cahn RG recording high-vacuum microbalance placed inside a temperature-controlled chamber, as described by Chiang and Sefton.[13]

The sample was evacuated for several days before each experiment and its initial weight recorded before it was lowered into the saturated vapor of bis-(2-chloroethyl)sulfide. The temperature of the sample and of the vapor source were controlled by a water jacket around the hang-down tube. The accuracy of the thermostat was better than ±0.2°C.

For the experiments with vapor activities less than unity, heat-degassed and distilled dioctylphthalate was mixed with bis-(2-chloroethyl)sulfide to obtain the desired vapor pressure. Dioctylphthalate, a compound of negligible vapor pressure, is known not to interact with the diffusant.

RESULTS AND DISCUSSION

Crystallinity

Rogers et al.[14] have shown that the solubility constant for several organic vapors in polyethylene decreases proportionally with increasing crystalline volume fraction of the polymer. Solution of molecules in completely crystalline regions of the polymer is not to be expected, and Michaels and Bixler[3] have expressed this as

$$S = \alpha S_A \qquad (8)$$

where α is the volume fraction of amorphous polymer and S_A the hypothetical solubility constant for the completely amorphous polymer.

Vieth and Wuerth[11] found that the solubility constant for polypropylene films annealed above 90°C followed the variation given by eq. (8), but all quenched films seemed to have the same solubility and the same amorphous content.

The results obtained for bis-(2-chloroethyl)sulfide in annealed polypropylene are plotted in Figure 1. The method used was not accurate enough to show the effect of temperature on the solubility in the rather narrow temperature range used in the experiments. However, the effect is small. This has often been reported for other organic vapor–polymer systems[2,15] and is a reflection of the low heat of mixing of the diffusant and the polymer.

The results in Figure 1 are in agreement with those found by Vieth and Wuerth[11] and also by Ochiai et al.[16] Films made by rapid cooling have a solubility significantly lower than what would be expected from the density. In quenched films a second crystalline phase is present, consisting of hexagonal crystals of an intermediate density, which on annealing are converted into the more stable, monoclinic crystal modification. Since the two-phase model does not apply to the quenched original material, corrections have to be made for amorphous volume fraction. Extrapolation in Figure 1 reduces the amorphous content of the original quenched material from 60 to 46%.

Michaels et al.[3,17] have expressed the diffusion coefficient for a diffusant in a semicrystalline polymer as
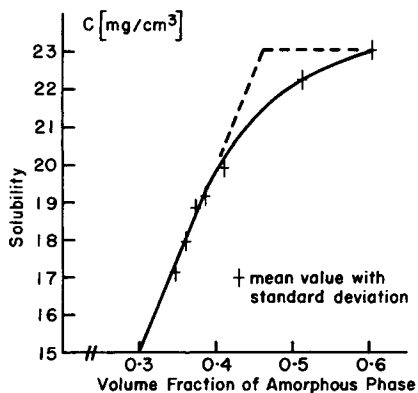
$$D = D^*/\tau\epsilon \qquad (9)$$

Fig. 1. The solubility of bis-(2-chloroethyl)sulfide in polypropylene plotted against the amorphous volume fraction over the temperature range 15–40°C.

where D^* is the diffusivity in the completely amorphous polymer, τ is a tortuosity factor to allow for the increased path length when diffusion occurs around crystallites, and ϵ is a chain immobilization factor to account for the restraining effect of crystallites on segmental mobility.

The diffusivity of bis-(2-chloroethyl)sulfide in the annealed polypropylene films was not found to be dependent on the crystalline volume fraction, at least not within the experimental error (Fig. 2)

The diffusivity was determined from the slope of the sorption curve by use of eq. (2). Since the amorphous content of the quenched original material is significantly lower than predicted from the two-phase theory by use of eq. (6), the range in crystallinity has been greatly narrowed. It is known that annealing leads to a decrease in the tortuosity factor due to an increase in fold length and therefore a decrease in the width-to-thickness ratio of the crystalline lamellae.[10,11] It is therefore likely that the immobilization of polymeric chains is counteracted by the increase in the tortuosity factor.

Vieth and Wuerth[11] observed the same constancy in the diffusion coefficient of gases in semicrystalline polypropylene but explained their results in terms of a reduction in impedance through formation of defects in the existing crystallites.

Solubility

The experimentally determined solubility of bis-(2-chloroethyl)sulfide in polypropylene is shown in Table I and the resulting isotherms in Figure 3.

The solubility c can be expressed as a function of the vapor pressures of the diffusant:

$$c = Sp \tag{10}$$

which turns into Henry's law when the solubility constant S is a function of temperature only. If the saturation pressure of the diffusant can be expressed by the integrated form of the Clausius-Clapeyron equation, eq. (10) can be written as follows:

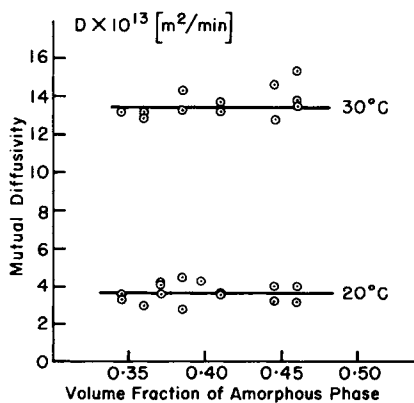$$c = Sp = S^1(p/p_0) \exp(-\Delta H_v/RT) = S^*p/p_0 \tag{11}$$

Fig. 2. The mutual diffusivity for the system bis-(2-chloroethyl)sulfide–polypropylene versus the amorphous content of the polymer.

Average Solubility and Standard Deviation of Vapor in the Amorphous Phase of Polypropylene at Different Vapor Activities Over the Temperature Range 15–40°C

Vapor Activity	Average Solubility, mg cm^{-3}
0.34	13.39 ± 0.85
0.49	18.98 ± 1.51
0.58	24.41 ± 1.26
0.68	30.46 ± 1.25
0.74	33.13 ± 1.72
0.85	39.50 ± 1.48
0.95	44.57 ± 0.76
1.00	50.09 ± 1.95

Here S^* is nearly independent of the temperature because the heat of condensation is of the same magnitude as the heat of solution.

The solubility constant can be represented by an empirical relation of the form

$$S^* = S_0^* \exp(\sigma c) \tag{12}$$

where S_0^* and σ are constants which are characteristic for the diffusant–polymer system and depend on the temperature. Relations similar to this equation have been reported for the solubility of many organic vapors in polyethylene.[14,15] Form the data in Table I, S_0^* and σ were determined by the least-squares method to be $S_0^* = 35.4$ mg cm^{-3} and $\sigma = 0.0068$ cm^3 mg^{-1}. Inserting these values into eq. (12) gives

$$S^* = 35.4 \exp(0.0068c) \tag{13}$$

The sorption isotherms of condensable vapors in polymers have often been found to be well represented by expressions based on the lattice theory of sol-
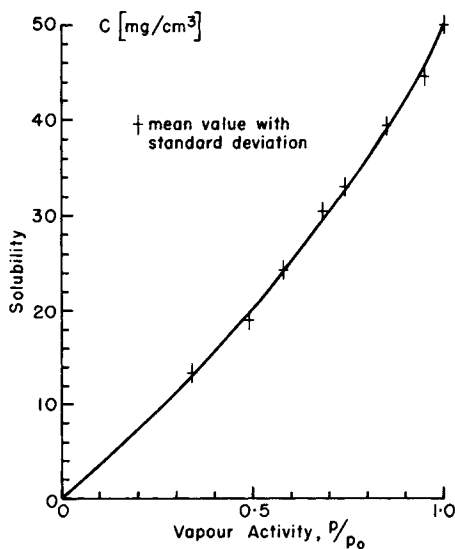

Fig. 3. The sorption isotherms of bis-(2-chloroethyl)sulfide in polypropylene over the temperature range 15–40°C.

vent–polymer solutions. Long and coworkers[18,19] have presented data for the sorption of several organic vapors in amorphous polymers, where the isotherms essentially obey the simplified form of the Flory-Huggins equation[20,21]:

$$\ln(p/p_0) = \ln(V_1) + V^2 + \chi V_2 \tag{14}$$

where V_1 and V_2 are the volume fraction of sorbed vapor and polymer, respectively, and χ is the Flory-Huggins interaction parameter.

The isotherms in Figure 3 cannot be represented satisfactorily by means of a single value of χ, even when the solubility is related only to the amorphous phase.

The value of the interaction parameters shows that there is only a weak interaction between bis-(2-chloroethyl)sulfide and polypropylene.

The interaction parameter in crosslinked polymer systems is assumed to be given by[22]

$$\chi = \mu + (\rho_a \overline{V}/M_c) V_2^{-5/3} \tag{15}$$

where μ is the interaction constant, ρ_a is the density of the amorphous polymer, $\overline{V}$ is the molar volume of the diffusant, and M_c is the average mol weight of crosslinked chains.

Curve fitting by the least-squares method of the data in Table II gives

$$\mu = 1.13$$

$$M_c = 155 \text{ g/mol}$$

when μ is assumed independent of the concentration. The value of M_c is of similar magnitude to values found for polypropylene[16] and polyethylene.[22] The high value of the interaction constant is an expression of the low affinity bis-(2-chloroethyl)sulfide has to polypropylene. Equation (14) can be rewritten in terms of mass concentration as follows[15]:

$$\ln \frac{p}{p_0} = \ln \left(\frac{c/\alpha\rho}{1 + c/\alpha\rho} \right) + \frac{1}{1 + c/\alpha\rho} + \chi \left(\frac{1}{1 + c/\alpha\rho} \right)^2 \tag{16}$$

where ρ is the density of the diffusant and α is the volume fraction of the amorphous phase. The solubility coefficient S^* can now be expressed as a function of χ by combining eqs. (11) and (16), when χ can be regarded as a constant:

$$\ln S^* = \ln(\alpha\rho) + \ln \left(1 + \frac{c}{\alpha\rho} \right) - \frac{1}{1 + c/\alpha\rho} - \chi \left(\frac{1}{1 + c/\alpha\rho} \right)^2 \tag{17}$$

TABLE II
Calculated Values of the Flory-Huggins Interaction Parameter Over the Temperature Range 15–40°C

p/p_0	V_1	V_2	χ
0.34	2.23×10^{-2}	0.9777	1.827
0.49	3.13×10^{-2}	0.9687	1.898
0.58	3.99×10^{-2}	0.9600	1.861
0.68	4.94×10^{-2}	0.9506	1.850
0.74	5.35×10^{-2}	0.9465	1.876
0.85	6.31×10^{-2}	0.9369	1.895
0.95	7.07×10^{-2}	0.9294	1.933
1.00	7.87×10^{-2}	0.9213	1.910

When $(c/\alpha\rho)^2 < 1$, the last three terms in the above equation can be expanded in series, and summation of terms then yields the expression

$$\ln S^* = -(1 + \chi) + \ln(\alpha\rho) + \sum_{n=1}^{\infty} (-1)^{n-1}(n + 1)\left(\frac{1}{n} + \chi\right)\left(\frac{c}{\alpha\rho}\right)^n \qquad (18)$$

At very low diffusant concentrations, when $c \to 0$, eq. (18) reduces to:

$$\ln S_0^* = -(1 + \chi) + \ln(\alpha\rho) \qquad (19)$$

Substituting eq. (19) into (18) yields

$$\ln S^* = \ln S_0^* + \sum_{n=1}^{\infty} (-1)^{n-1}(n + 1)\left(\frac{1}{n} + \chi\right)\left(\frac{c}{\alpha\rho}\right)^n \qquad (20)$$

When $c/\alpha\rho$ is small, only the first term is necessary:

$$S^* = S_0^* \exp\left(2(1 + \chi)\frac{c}{\alpha\rho}\right) \qquad (21)$$

Equation (21) has the same form as the empirical eq. (12), and a comparison of the two shows that

$$\sigma = (2/\alpha\rho)(1 + \chi) \qquad (22)$$

By using the mean value of 1.87 for the interaction parameter, one obtains, from eqs. (19) and (22):

$$S_0^* = 33.2 \text{ mg/cm}^3$$

$$\sigma = 0.0098 \text{ cm}^3/\text{mg}$$

which are in satisfactory agreement with the experimentally determined values in eq. (13), considering the assumptions made.

Diffusivity

It is believed that the kinetics of sorption in amorphous polymers in invariably Fickian well above the glass transition temperature T_g.[1,5] But several cases of sigmoid sorption curves have been obtained in crystalline polymers above T_g, and the sigmoid character is more pronounced at higher crystallinities.[8,9,14] It appears likely that this often-observed effect in crystalline polymers is due to time-dependent responses to external changes.

Typical reduced absorption curves for bis-(2-chloroethyl) sulfide in polypropylene are shown in Figure 4 for four different vapor activities. In all cases they are found to be linear in the initial stage of the absorption process. In fact the linear part extends to more than 80% of the M_∞ value, and above that, they are concave to the abscissa. These are requirements for Fickian-type diffusion, together with the requirement that the reduced absorption curves for different film thicknesses are superimposable on a single curve when plotted against $(t/l^2)^{1/2}$. Due to the small range in thickness of the samples (25–30 μm), this criterion has not been verified, but the sorption is treated as Fickian. It is assumed that the low solubility of bis-(2-chloroethyl)sulfide in the polymer together with the fairly low diffusion rate do not create relaxation problems for the polymer.

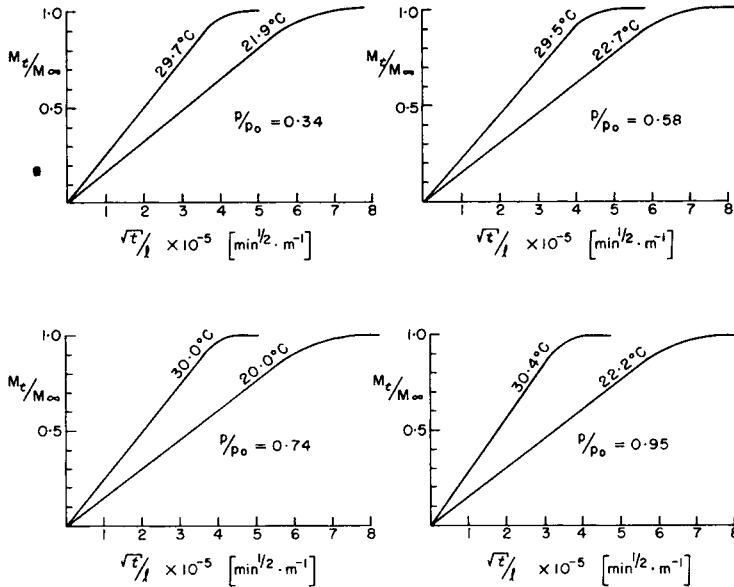The mutual diffusion coefficient, determined from eq. (2), is plotted against

Fig. 4. Reduced sorption curves for the system bis-(2-chloroethyl)sulfide–polypropylene at four different vapor activities.

$1/T$ in Figure 5. It is seen from the graph that the mutual diffusion is independent of concentration, at least within experimental error. This also justifies
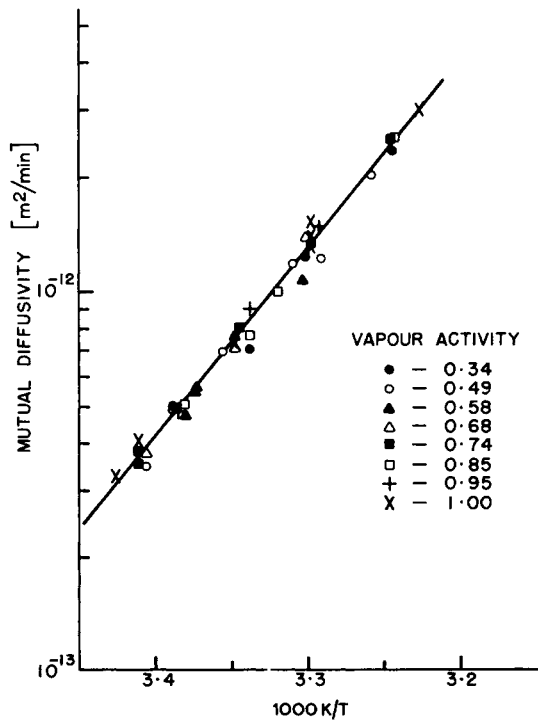

Fig. 5. The mutual diffusivity of bis-(2-chloroethyl)sulfide in polypropylene at different vapor activities versus $1/T$.

basing the diffusivity only on the initial slope of the absorption curve without taking the desorption into consideration.

This is in contrast to what has been found for most polymer–organic vapor systems, where the diffusivity is often exponentially dependent on the diffusant concentration.

The low solubility of bis-(2-chloroethyl)sulfide in polypropylene and the high value found for the Flory-Huggins interaction parameter also show that the plasticizing effect of the diffusant would be small. Therefore, the diffusant is not likely to increase the mobility of the polymeric chains significantly. Rogers and coworkers[14] have shown that the more strongly the diffusant interacts with the polymer, the more concentration dependent the diffusivity will be.

Fujita and Kishimoto[23] found the diffusity of water in polyvinyl acetate and polymethyl acrylate to be concentration independent with low solubility and high values of the Flory-Huggins interaction parameter. Almost concentra-tion-independent mutual diffusion coefficients have also been found for the diffusion of halotane and methoxyfluorane in silicone rubber.[15]

In Figure 6 the mutual diffusivity has been corrected for swelling, eq. (4). The validity of this equation is believed to be justified, since all the data refer to the original material with no additional treatment which could cause void defects. One observes that the intrinsic diffusivity increased slightly with concentration. The mutual diffusion coefficient is equal to the intrinsic diffusivity at zero concentration. The concentration dependence to the diffusivity does not depend on the temperature. This can also be seen from the left-hand side of Table III.

The apparent activation energy for the diffusion process is also found to be constant within experimental error. It is defined as

$$\Delta H = -R \frac{d(\ln D)}{d(1/T)} \qquad (23)$$

and is found from the slope of Figure 5 to be 22.5 kcal mol^{-1}.

In spite of the low concentration dependence found for the intrinsic diffusivity, the results are examined in terms of Fujita's free-volume theory.[2,5,24] The basic assumption of this free-volume theory is summarized by the equation

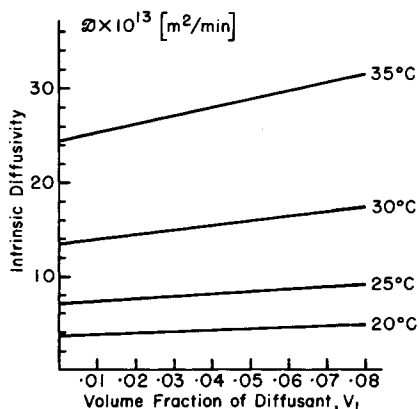$$\mathcal{D}_T = RTA_0 \exp(-B_0/f_v) \qquad (24)$$

Fig. 6. The diffusivity of bis-(2-chloroethyl)sulfide in polypropylene corrected for swelling.

TABLE III
Values of the Parameters in Eqs. (26) and (27)

V_1	$\mathcal{D}/\mathcal{D}_0$	χ	$\mathcal{D}_T/\mathcal{D}$	$\mathcal{D}_T/\mathcal{D}_0$	t, °C	$\mathcal{D}_0 \times 10^{13}$, m²/min	$f_0 \times 10^2$	$\ln(\mathcal{D}_0/RT)$
0.01	1.031	1.83	1.048	1.081	20	3.7	4.32	−35.00
0.02	1.063	1.84	1.101	1.171	25	7.2	4.56	−34.34
0.03	1.096	1.86	1.160	1.271	30	13.4	4.80	−33.74
0.04	1.130	1.87	1.225	1.385	35	24.5	5.04	−33.15
0.05	1.166	1.88	1.297	1.512	40	44.5	5.28	−32.57
0.06	1.204	1.89	1.376	1.657				
0.07	1.243	1.91	1.468	1.824				
0.08	1.284	1.92	1.570	2.015				

where A_0 and B_0 are parameters which are assumed to be independent of diffusant concentration. The term f_v is the fractional free volume of the system and for small values of V_1 can be written

$$f_v = f_0 + \beta V_1 \tag{25}$$

where f_0 is the fractional free volume in the pure polymer and β is a function of the temperature.

By combining these two equations, we obtain

$$\ln(\mathcal{D}_0/RT) = \ln A_0 - B_0/f_0 \tag{26}$$

$$[\ln(\mathcal{D}_T/\mathcal{D}_0)]^{-1} = f_0/B_0 + f_0^2/B_0\beta V_1 \tag{27}$$

Here $\mathcal{D}_0$ is the limiting value of $\mathcal{D}_T$ for zero diffusant concentration and equal to the mutual diffusivity at the same limit.

The thermodynamic diffusion coefficient is obtained as a function of V_1 from the relationship

$$\mathcal{D}/\mathcal{D}_T = (1 - V_1)(1 - 2\chi V_1) \tag{28}$$

found by combining eqs. (5) and (14) and differentiating. According to eq. (27), a plot of $[\ln(\mathcal{D}_T/\mathcal{D}_0)]^{-1}$ versus V_1^{-1} should give a straight line. Such a plot is shown in Figure 7 based on the data in Table III. The plot is linear over the whole range of V_1. It is also observed that the plot is independent of the temperature because the solubility was found to be independent of the temperature and because the mutual diffusivity was constant within the accuracy of the experiment and equal to $\mathcal{D}_0$. The same observation has been made by Suwandi and Stern[15] but explained to be caused by the very low glass transition temperature in their system.

From the slope of the straight line in Figure 7 one can calculate $B_0\beta$, when the free volume of the polymer is known. It is generally argued that the temperature dependence of f_0 is given by[25]

$$f_0 = 0.025 + 4.8 \times 10^{-4}(t - t_g) \tag{29}$$

where t_g is the glass transition temperature for the polymer, which for polypropylene is −18°C.[26] This equation is combined with the slope of Figure 5 and fitted to a straight line by the least-squares method to give

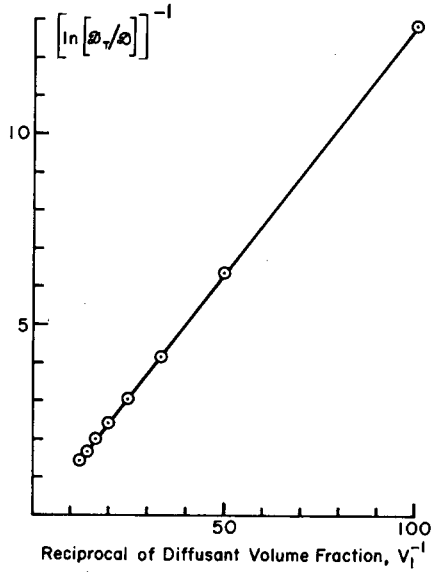$$B_0\beta = 6.72 \times 10^{-4} + 3.56 \times 10^{-4}(t - t_g) \tag{30}$$

Fig. 7. $[\ln(\mathcal{D}_T/\mathcal{D}_0)]^{-1}$ as a function of the reciprocal volume fraction of bis-(2-chloroethyl)sulfide in polypropylene.

The intercept in Figure 7 is too small to be used to determine the value of B_0, but this parameter can be found from eq. (26), plotted in Figure 8. The data are well fitted to a straight line, giving $B_0 = 0.58$ and $A_0 = 3.7 \times 10^{-10}$ m^2 mol min^{-1} cal^{-1}.

The value obtained for B_0 is in the range of what has been found for other polymer–organic vapor systems. This parameter has been found to be rather insensitive to the polymer type, and values ranging from 0.63 to 0.89 have been reported for widely different polymers.[27]

Inserting A_0, B_0, and f_0 into the eqs. (24) and (25) gives the expressions for the diffusivity and the free volume of bis-(2-chloroethyl)sulfide in polypropylene:
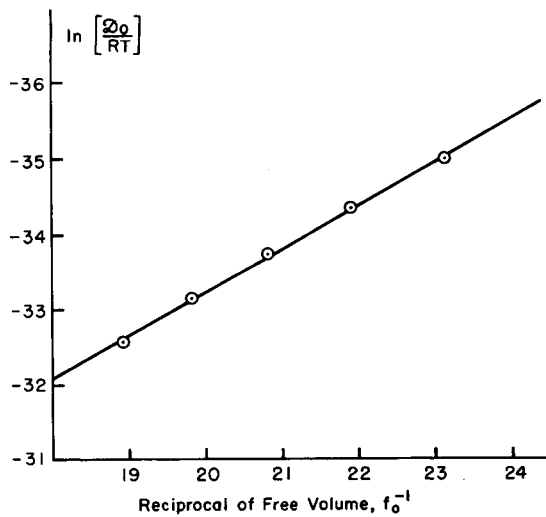

Fig. 8. $\ln(\mathcal{D}_0/RT)$ plotted as a function of the reciprocal free volume of bis-(2-chloroethyl)sulfide in polypropylene.

$$f_v = 0.025 + 4.8 \times 10^{-4}(t - t_g) + [1.16 \times 10^{-3} + 6.14 \times 10^{-4}(t - t_g)]V_1$$

(31)

and

$$\mathcal{D}_T = 3.7 \times 10^{10}RT \exp(-0.58/f_v)$$

(32)

It has been shown that diffusion of bis-(2-chloroethyl)sulfide in polypropylene in general follows the normal pattern. The error introduced by regarding the diffusivity independent of the concentration is small, and the permeation process is well described by the appropriate solution of the diffusion equation.

References

1. P. J. Mears, *J. Appl. Polym. Sci.*, **9**, 917 (1965).
2. H. Fujita, A. Kishimoto, and K. Matsumoto, *Trans. Faraday Soc.*, **56**, 424 (1960).
3. A. S. Michaels and H. J. Bixler, *J. Polym. Sci.*, **50**, 393 (1961).
4. J. Crank, *The Mathematics of Diffusion*, Oxford University Press, London, 1956.
5. H. Fujita, *Diffusion in Polymers*, Academic, New York, 1968, p. 75.
6. G. S. Hartley and J. Crank, *Trans. Faraday Soc.*, **45**, 801 (1949).
7. D. R. Paul, *J. Appl. Polym. Sci.*, **18**, 473 (1974).
8. P. Mears, *J. Polym. Sci.*, **27**, 405 (1958).
9. A. Kishimoto and K. Matsumoto, *J. Polym. Sci., Part A*, **2**, 679 (1969).
10. D. A. Blackadder and J. S. Keniry, *Makromol. Chem.*, **141**, 211 (1971).
11. W. Vieth and W. F. Wuerth, *J. Appl. Polym. Sci.*, **13**, 685 (1969).
12. E. W. Balson, K. G. Denbigh, and N. K. Adam, *Trans. Faraday Soc.*, **43**, 42 (1947).
13. K. T. Chiang, and M. V. Sefton, *J. Polym. Sci.*, **15**, 1927 (1977).
14. C. E. Rogers, V. Stannet, and W. Szwarc, *J. Polym. Sci.*, **45**, 61 (1960).
15. U. S. Suwandi and S. A. Stern, *J. Polym. Sci.*, **11**, 663 (1973).
16. H. Ochiai, K. Gekko, and H. Yamamura, *J. Polym. Sci.*, **9**, 1629 (1971).
17. A. S. Michaels, H. J. Bixler, and H. L. Fein, *J. Appl. Phys.*, **35**, 3165 (1964).
18. R. J. Kokes, A. R. DiPietro, and F. A. Long, *J. Am. Chem. Soc.*, **75**, 6319 (1953).
19. S. Prager and F. A. Long, *J. Am. Chem. Soc.*, **73**, 4072 (1951).
20. P. J. Flory, *J. Chem. Phys.*, **9**, 660 (1941).
21. M. L. Huggins, *J. Chem. Phys.*, **9**, 440 (1941).
22. C. E. Rogers, V. Stannet, and M. Szwarc, *J. Phys. Chem.*, **63**, 1406 (1959).
23. H. Fujita and A. Kishimoto, *J. Polym. Sci.*, **28**, 547 (1958).
24. H. Fujita, *Fortschr. Hochpolym. Forsch.*, **3**, 1 (1966).
25. M. L. Williams, R. F. Landel, and J. D. Ferry, *J. Am. Chem. Soc.*, **77**, 361 (1955).
26. J. Bromdrup and E. H. Immergut, *Polymer Handbook*, 2nd ed., Wiley, New York, 1975.
27. T. A. Garrett and G. S. Park, *J. Polym. Sci.*, **16**, 601 (1967).