

Solubility and Diffusion Coefficient of Antioxidants in Polyethylene

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Synopsis

As an aid in assessing the ability of antioxidant additives to persist in polymers and thus remain effective in protecting against oxidation, the solubility and diffusion coefficient of two antioxidants in branched polyethylene have been determined in this work. A method was developed for this purpose by which the diffusion coefficient and solubility could be determined simultaneously. The method consists of analyzing the concentration profile across a stack of polyethylene sheets through which the antioxidant was allowed to diffuse. The concentration of antioxidants in polyethylene was determined by a thermogravimetric technique which relies directly on the ability of the additives to suppress oxidation reaction. The diffusion coefficients determined showed excellent agreement with values in the literature which were obtained by a radiotracer method. The solubility of the antioxidants in three normal hydrocarbon solvents of varying molecular sizes was also determined by a conventional technique at various temperatures and found to correlate well with their solubility in polyethylene determined by the diffusion method. In particular, the dependence of the solubility on the size of solvent molecules and on temperature agrees well with an equation derived on the basis of the regular solution theory of liquid mixtures.

INTRODUCTION

For protection of polyolefins and other plastics against thermal oxidation, it is customary to add a small amount of antioxidant into the polymer. Effectiveness of such an antioxidant depends not only on the chemical nature of the antioxidant but also on its ability to persist in the polymer throughout the intended lifetime under a variety of use conditions. The basic physical quantities that control the retention of the antioxidant in the polymer are its diffusion coefficient and the solubility in the polymer. The knowledge of the solubility is required also in understanding the kinetics of the reactions by which the additive scavenges the oxidation process.

Diffusion coefficients of several antioxidants in polyethylene and polypropylene were previously measured by Jackson, Oldland and Pajaczowski¹ by a radioactive tracer technique. In the present work, we have devised a new method of measuring the diffusion coefficient and solubility of an antioxidant in a polymer simultaneously. The method does not require the preparation of radioactive additives and therefore can be more versatile. In this work, we apply the technique to the study of two antioxidants in branched polyethylene.

In addition to determining the solubility of the antioxidants in polyethylene by the above technique, we have also measured their solubility in normal hydrocarbon liquids by a conventional method. The solubility of a substance in these media, all similar in chemical nature but differing in chain length, can be correlated with each other on the basis of one of the theories of liquid mixtures; and in this work, we utilize the regular solution theory with the Flory-Huggins entropy of mixing. The solubility data, obtained as a function of temperature and the size of the hydrocarbon solvent molecules, were analyzed in terms of a relation derived from the regular solution theory to ascertain the factors governing the solubility of antioxidants in polyethylene.

EXPERIMENTAL

Materials

The antioxidants chosen for this work are 4,4'-thiobis(3-methyl-6-*tert*-butylphenol) and tetrakis[methylene-3-(3',5'-di-*tert*-butyl-4-hydroxyphenyl)propionate]methane, and will be referred to hereafter as Phenol A and Phenol B, respectively.

The branched polyethylene used is the product of Union Carbide Corporation, designated as DYNK, and is free from additives. It was used without further purification and molded into sheets 5 mils thick by heating it to 170°C in a press and then rapidly cooling to room temperature in 3.5 min. The density of the sheets thus prepared was 0.9175 g/cc, which corresponds to 48% crystallinity.

The normal hydrocarbons employed as lower homologs of polyethylene are *n*-octane (C₈H₁₈), *n*-hexadecane (C₁₆H₃₄), and *n*-octacosane (C₂₈H₅₈, mp 61.5°C) of 99% purity and used as received without further purification.

Measurement of Solubility in Hydrocarbon Liquids

For measurement of the solubility of the antioxidants in normal hydrocarbons, a test tube containing weighed amounts of the solvent and solute was slowly heated until the antioxidant dissolved completely in the liquid. By illuminating the test tube from behind, it was possible to see the floating antioxidant powder clearly; and with a slow heating rate, the dissolution temperature could be reproduced within $\pm 1^\circ\text{C}$ in most cases.

Analysis of Antioxidant Concentration in Polyethylene

For quantitative determination of the concentrations of antioxidants in polyethylene that are required for the analysis of diffusion data to be described below, we developed a thermogravimetric technique (TGA) that directly utilizes the ability of antioxidants to suppress an oxidation reaction. In this method, a small amount (ca. 4 mg) of the polyethylene sample containing an antioxidant is heated rapidly (at 160°C/min) to a fixed temperature (typically 200°C) in oxygen, and the change in the weight of the sample is monitored as a function of time. Figure 1 illus-

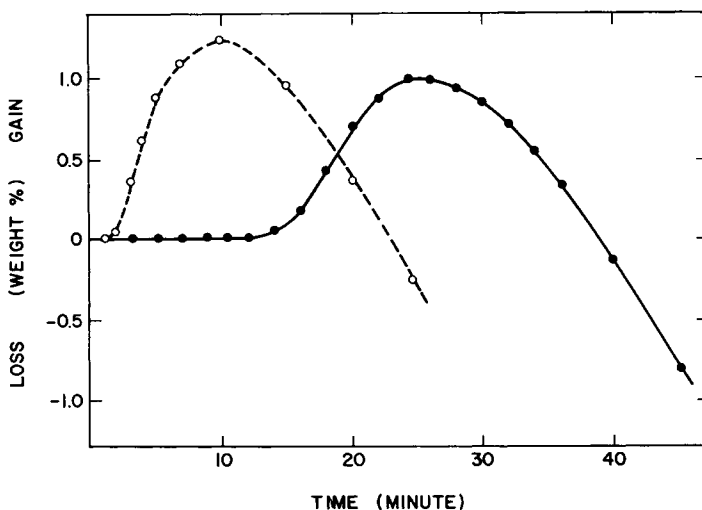


Fig. 1. Typical results of thermogravimetric analysis (TGA) of oxidation of polyethylene with and without antioxidant. Broken line: without antioxidant; solid line: polyethylene with 0.02 wt-% Phenol B.

trates the course of such weight changes exhibited by two samples, one with and the other without an antioxidant. The branched polyethylene containing no antioxidant begins to absorb oxygen rapidly 1.5 min after being heated to 200°C, and its weight increases. As the oxidation products begin to decompose, volatile components are liberated, causing a maximum in weight at about 10 min.

When the polyethylene contains an antioxidant, the onset of the initial weight gain is preceded by an induction period in which the weight remains constant. At constant temperature, the induction period is found to be proportional to the concentration of the antioxidant in the polymer. Although polyethylene with 0.02% Phenol B has an increase in the induction period of 13.5 min over the unprotected polymer, the shape of the two TGA curves is similar. Note in Figure 1 that the slope (rate of weight loss) of the trailing edge of both curves is identical.

From a study of the induction period of samples containing known amounts of antioxidant varying in concentration from 0.005% to 0.10% (by weight), a calibration curve was constructed for both Phenol A and B. At 200°C, the induction time ranges from 9 (or 6) min at concentration of 0.005% to 42 (or 38) min at 0.04% Phenol A (or Phenol B). The method is capable of detecting antioxidants at concentrations above 0.001 wt-%. It is thus superior to other conventional techniques such as IR and UV spectroscopy² and gas and liquid chromatography.

Measurement of Diffusion Coefficient and Solubility in Polyethylene

The simultaneous measurement of solubility and diffusion coefficient of an antioxidant in polyethylene is achieved by analyzing the concentration profile that exists when the antioxidant has diffused through a stack of

polyethylene films. The experimental setup is depicted schematically in Figure 2.

Molded discs of polyethylene without antioxidant, 5 mils thick and 2 in. in diameter, are stacked in the center of the diffusion device. Between 13 and 27 discs are employed at a run. A disc 2 in. in diameter and 60 mils thick, molded from the same polyethylene but containing 2 wt-% of the antioxidant, is placed above and below the stack and serves as a reservoir of antioxidant. The assembly is clamped between two heavy brass plates, and a pressure of about 30 psi is applied to the polyethylene through six bolts fitted with compression spring sleeves. The whole device is now placed in a vacuum oven for a period of time at a constant temperature. As time elapses, the excess antioxidant originally contained in the thicker, outer discs exudes out and diffuses into the thinner, inner discs. At the end of the run, the polyethylene discs are peeled apart, and the concentration of the antioxidant in each disc is analyzed by the thermogravimetric method. The primary data thus obtained are the values of concentration as a function of position after a fixed length of time. By comparing the concentration profile with master curves obtained by solution of the diffusion equation with appropriate boundary conditions, one can determine the solubility and the diffusion coefficient, as described in detail below.

In the diffusion cell depicted in Figure 2, we have a diffusion process within a solid bounded by two parallel surfaces which are very large in area compared to the distance between the surfaces. The concentration of antioxidant within the solid interior is zero initially, while the concen-

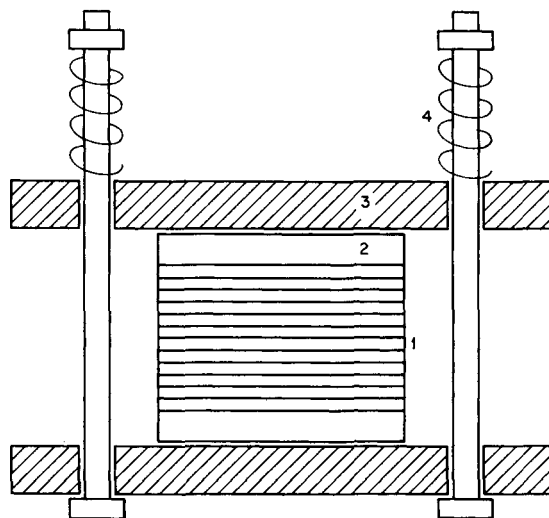


Fig. 2. Schematic illustration of diffusion cell: (1) stack of polyethylene sheets, each 5 mil thick and 2 in. in diameter; (2) polyethylene discs $\frac{1}{8}$ in. thick, containing large excess of antioxidant; (3) brass plates; (4) bolts and nuts with compression springs.

tration at the surface is maintained essentially at the equilibrium solubility because of the large excess of antioxidant available in the outer, thicker discs. The solution of Fick's diffusion equation under the above boundary conditions (with the diffusion coefficient D independent of concentration) is³

$$C(x,t) = C_0 - \frac{4}{\pi} C_0 \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} e^{-(2n+1)^2 \pi^2 K/4} \cos \frac{(2n+1)\pi x}{2l} \quad (1)$$

where $2l$ is the total thickness of the stack of thin discs, x is the position coordinate with the origin at the center of the stack, $C(x,t)$ is the concentration of antioxidant at position x at time t , C_0 is the equilibrium solubility, and K is given by

$$K = Dt/l^2. \quad (2)$$

A semilog plot of $C(x,t)/C_0$ against x/l calculated for a number of values of K is shown in Figure 3.

The concentration of antioxidant determined experimentally is plotted on similar semilog paper against x/l , where x is taken to be the coordinate of the center of each 5-mil disc. An example of such a plot is shown in Figure 4. The first and last thin discs were not analyzed for concentration because of the possibility of physical contamination of their outer surfaces by antioxidant from the reservoir discs. The experimental plot such as

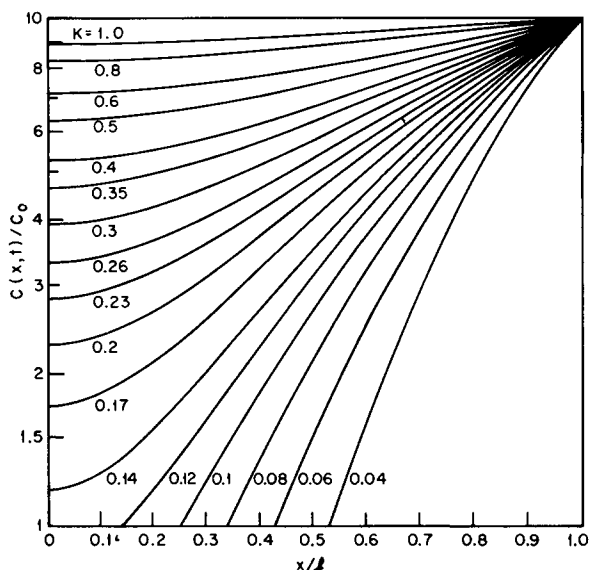


Fig. 3. Solutions of diffusion equation with boundary conditions corresponding to those prevailing in the cell shown in Fig. 2: x is the position coordinate from the center of the polyethylene stack; l is half the total thickness of the stack; $C(x,t)$ is the concentration at position x at time t ; C_0 is the equilibrium solubility. The curves are calculated for different values of K indicated, where $K = Dt/l^2$.

Figure 4 is then overlaid on the computed set of curves in Figure 3, and the best match of all the points to a single curve is found by sliding the plot vertically. From the amount of vertical shift one can then calculate the solubility C_0 , while from the value of K of the best matching curve one can obtain D according to eq. (2).

The sensitivity for the determination of D is best when K is in the vicinity of 0.15, while C_0 can be determined more accurately at larger values of K . The duration time of diffusion and the number of 5-mil discs (hence l) were adjusted for each run so as to give a K value of 0.2–0.3 whenever an approximate estimate of D was possible. The diffusion time t allowed varied from 66 hr with Phenol A at 68°C to 480 hr with Phenol B at 56°C.

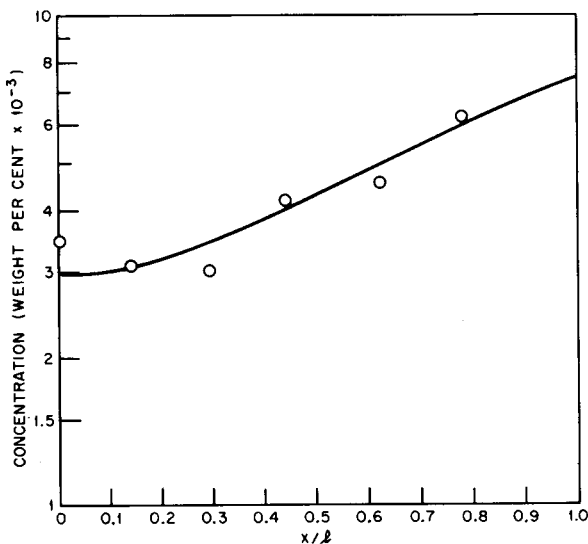


Fig. 4. Example of concentration profile across the stack of polyethylene sheets, which was attained after Phenol A had been allowed to diffuse for 11 days at 45°C. Solid curve is the solution of diffusion equation with $K = 0.3$ as shown in Fig. 3. The solubility is given by the value of the theoretical curve at $x/l = 1.0$.

Although the polyethylene discs were compressed under 30 psi of pressure, gaps might still exist between the discs which offer a resistance to diffusion of antioxidant. To examine the possibility of such an effect, we made a control experiment in which we replaced most of the 5-mil discs with a few 20-mil discs while maintaining the overall thickness of the stack fixed. A diffusion experiment with this modified stack was performed side by side in the same oven with a regular setup consisting of 5-mil discs only. The result obtained from the control experiment was identical within experimental error with that obtained with the regular experiment. This result indicates that either no gaps exist between polyethylene sheets, or antioxidant is transported readily through the vapor phase across the gaps when the gaps exist.

RESULTS AND DISCUSSION

Figure 5 shows the values of the diffusion coefficient of Phenol A and B obtained at three temperatures. The straight lines drawn in the figure correspond to an activation energy of 12.4 kcal/mole, which was obtained previously by Jackson, Oldland, and Pajaczkowski¹ from measurement of diffusion of a few antioxidants in branched polyethylene by a radioactive tracer technique. The agreement with our data is excellent. Phenol B (mol wt 1178) is a much bigger molecule than Phenol A (mol wt 358), and the difference in molecular size is reflected in the large difference in the diffusion coefficients. The values of the diffusion coefficients of several other antioxidants in branched polyethylene are reported in the literature^{1,4} and are summarized in Table I. In Figure 6 we plot the diffusion coefficients at 67°C of these antioxidants and *n*-octadecane against the molecular weight on log-log paper. One would expect that the diffusion coefficient depends not only on the molecular weight but also on the shape of the molecule and the degree of mutual interaction, and it is therefore not surprising that in Figure 6 there is no well-defined correlation between the molecular weight and *D*. The diffusion coefficient of *n*-octadecane is much higher than those of the other substances, probably because unlike the polar anti-

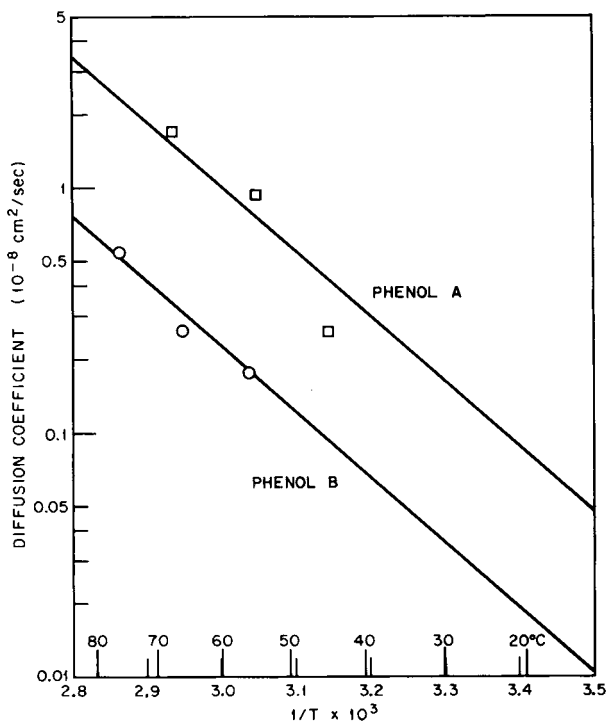


Fig. 5. Observed diffusion coefficients plotted against reciprocal absolute temperature. The two straight lines are drawn with a slope corresponding to the activation energy of 12.4 kcal/mole.

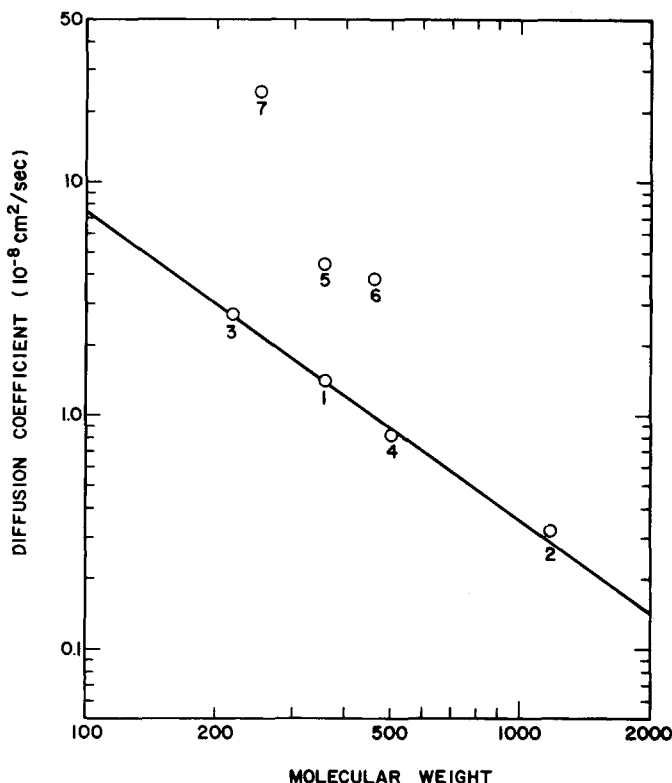


Fig. 6. Diffusion coefficients of several antioxidants and *n*-octadecane in polyethylene plotted against molecular weight. For identification of individual compounds, refer to indicated numbers in Table I. A linear relation in the log-log plot is obtained with four antioxidants which all belong to the class of hindered phenols.

oxidants it lacks a tendency for association. Of the six antioxidants shown, the diffusion coefficients of four fall on a straight line drawn in Figure 6, which can be described by

$$D = 3.46 \times 10^{-5} (\text{mol wt})^{-1.33}. \quad (3)$$

The remaining two antioxidants show values of D higher by a factor of 3 to 4. It may be significant that those four antioxidants showing the straight-line correlation are all hindered phenols, which probably exhibit similar degrees of association. In view of the limited amount of data available, however, it is difficult to say whether the correlation expressed in eq. (3) has any wider applicability.

Table II lists the solubilities of Phenol A and Phenol B determined by the diffusion method. The precision of the solubility values determined by the method is somewhat less than that for the diffusion coefficient. This is because one needs to know only the relative variation of concentration in

TABLE I
Diffusion Constants of Antioxidants in Polyethylene

Additive no.	Additive name	Mol wt	D at 67°C, 10^{-8} cm ² /sec	Source
1	Phenol A	358	1.4	this work
2	Phenol B	1178	0.32	this work
3	2,6-di- <i>tert</i> -butyl- <i>p</i> -cresol	220	2.7	ref. 4
4	Phenol C ^a	509	0.81	ref. 1
5	<i>n</i> -ODE ^b	356	4.4	ref. 1
6	DLTP ^c	467	3.8	ref. 1
7	<i>n</i> -Octadecane	255	24.	ref. 5

^a 1,1,3-Tri[2-methyl-4-hydroxy-5-(*tert*-butyl)phenyl]butane.

^b *n*-Octadecyldiethanolamine.

^c Didodecyl 3,3'-thiodipropionate.

the determination of a diffusion coefficient, while an absolute value of concentration is required for the solubility. The accurate determination of antioxidant concentration in polyethylene at levels below 1 part in 10,000 is difficult. In the section which follows, it will be shown that the measured concentrations of antioxidant are always within a factor of 2 of the solubility values predicted on the basis of the data in lower molecular weight hydrocarbon solvents.

TABLE II
Solubility of Antioxidants in Polyethylene Determined by the Diffusion Method

Temp., °C	Solubility, wt-%	
	Phenol A	Phenol B
45	0.0074	—
55	0.0090	—
56	—	0.0029
66	—	0.0091
68	0.0140	—
76	—	0.0111

Figures 7 and 8 show the solubilities of Phenol A and Phenol B, respectively, in the hydrocarbon solvents, determined by the visual method. Here, the higher precision of measurement attained allows us to determine the temperature dependence of the solubility. The three solid straight lines drawn in each of the figures are parallel to each other and can be represented by

$$-\ln w_1 = a/T - b \quad (4)$$

where w_1 is the solubility expressed as weight per cent of solute, and the values of a and b are listed in Table III.

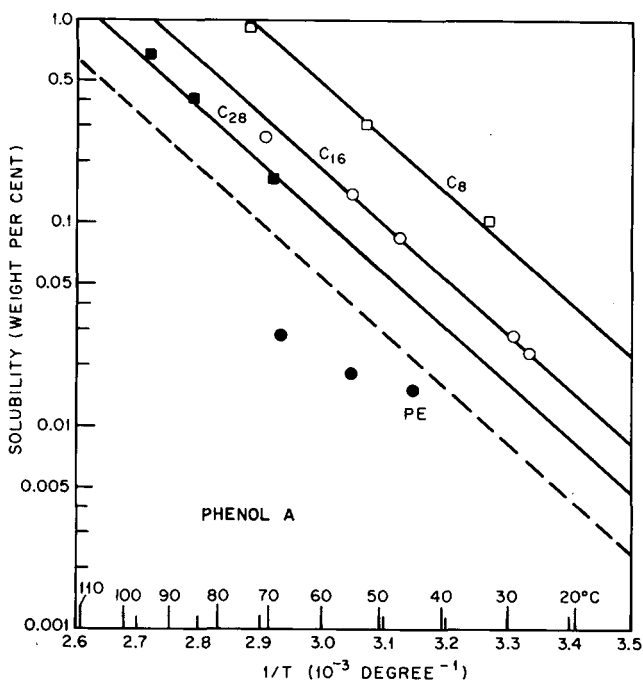


Fig. 7. Solubility of Phenol A in hydrocarbon media presented here as a function of temperature and size of hydrocarbon solvent molecules. Filled circles shown as the solubility in polyethylene were taken from the solubility data obtained by the diffusion experiment (see Table II), but were multiplied by 2 to correct for the degree of crystallinity (around 50%). Broken line is the solubility of Phenol A in polyethylene predicted from the regular solution theory on the basis of its solubility in lower hydrocarbon solvents.

The solubility of a solid in a liquid is determined by the condition that the molar free energy of fusion, ΔF_f , of the solid is exactly compensated by the partial molar free energy of mixing, $\overline{\Delta F}_m$, of the molten solute with the solvent. The former can be expressed as

$$-\Delta F_f = \Delta H_f(1 - T/T_m) \quad (5)$$

where ΔH_f is the heat of fusion per mole and T_m is the melting temperature. Within the framework of the regular solution theory,^{6,7} the partial molar free energy of mixing is given by

$$\overline{\Delta F}_m = RT[\ln \Phi_1 + (1 - V_1/V_2)\Phi_2 + \chi_1\Phi_2^2] \quad (6)$$

where Φ_1 and Φ_2 are the volume fractions, V_1 and V_2 are the molar volumes of the solute and solvent, respectively, and χ_1 is the solvent-solute interaction parameter. By equating the sum of (5) and (6) to zero and setting $\Phi_2 \approx 1$, we obtain

$$-\ln \Phi_1 = \frac{\Delta H_f}{R} \left(\frac{1}{T} - \frac{1}{T_m} \right) + \left(1 - \frac{V_1}{V_2} \right) + \chi_1. \quad (7)$$

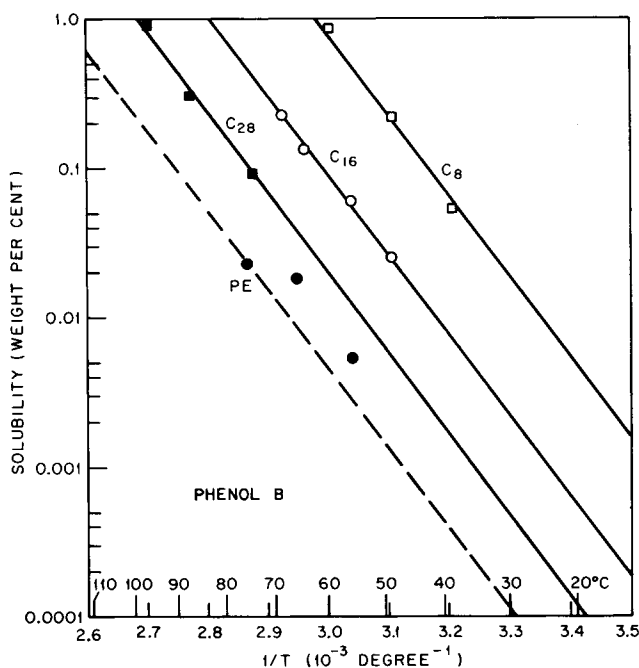


Fig. 8. Solubility of Phenol B in hydrocarbon media. See caption to Fig. 7 for explanation.

Physical quantities appearing in eq. (7), except χ_1 , are known and are tabulated in Tables III and IV.

The value of χ_1 , which is a measure of the specific interaction between the solute and solvent molecules, is expected for a given antioxidant to be fairly independent of the length of the hydrocarbon solvent molecules. The fact that the data for different solvents shown in Figures 7 and 8 are parallel to each other gives support to this view. It then follows that the only

TABLE III
Summary of Solubility Data in Hydrocarbon Liquids

Solvent	<i>n</i> -Octane	<i>n</i> -Hexadecane	<i>n</i> -Octacosane
Mol wt	114.23	226.45	394.77
Density at 20°C	0.7025	0.7733	0.807 ^a
Mol. volume, cc/mole	162.6	292.8	489.2
Phenol A			
<i>a</i> in eq. (4)	6.14×10^3	6.14×10^3	6.14×10^3
<i>b</i> in eq. (4)	17.67	16.70	16.15
Solubility at 23°C, wt-%	0.047	0.0178	0.0103
Phenol B			
<i>a</i> in eq. (4)	12.30×10^3	12.30×10^3	12.30×10^3
<i>b</i> in eq. (4)	36.63	34.48	32.97
Solubility at 23°C, wt-%	0.0075	0.00087	0.000192

^a Supercooled liquid, estimated by extrapolation.

TABLE IV
Molecular Parameters of Antioxidants Studied

	Phenol A	Phenol B
Mol wt, g/mole	358	1178
Density, g/cc	1.095	1.13
Molar volume, cc/mole	327	1042
Melting point, °C	164	122.8
Heat of fusion		
cal/g	24.2	13.9
kcal/mole	8.66	16.4

quantity in eq. (7) that depends on the size of the solvent molecule is the term V_1/V_2 . A plot of the logarithm of the solubility against the reciprocal of the molar volume of solvent is therefore expected to yield a linear relation. Such plots for both Phenol A and Phenol B are shown in Figure 9 (the solu-

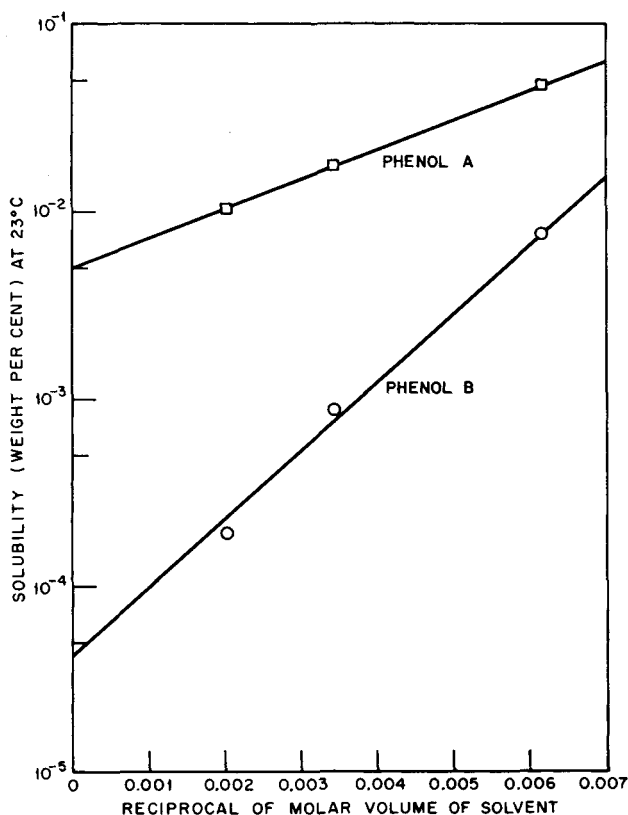


Fig. 9. Solubility of antioxidants at 23°C plotted against reciprocal molar volume of the hydrocarbon solvent molecules. From the slopes of the linear relation one can, in accordance with the regular solution theory, derive the molar volumes of Phenol A and Phenol B to be 331 and 808 cc/mole, respectively, which is in good agreement with the values 325 and 1042 calculated from the chemical formula and density.

bility values are those at 23°C obtained by extrapolation from Figs. 7 and 8). The much higher slope in Figure 9 for Phenol B than for Phenol A reflects the larger size of the former. Indeed, from the slopes (after applying a correction for the small difference between the volume and weight fractions), we determined the values of V_1 to be 331 and 808 cc/mole for Phenol A and Phenol B, respectively, in satisfactory agreement with the values 325 and 1042 cc/mole calculated from the chemical formula and density.

In Figure 9, extrapolation to $1/V_2 = 0$ establishes the solubility of the two antioxidants in polyethylene at 23°C. The broken lines in Figures 6 and 7 are drawn to pass through these solubility values at 23°C and parallel to the solubility data in other lower hydrocarbon solvents. Also shown in these figures are the observed solubilities in polyethylene multiplied by 2. The factor of 2 is necessary because the polyethylene samples we used were about 50% crystalline. Although the observed values deviate from the expected values shown by the broken lines sometimes by as much as a factor of 2, the agreement is still considered very satisfactory, especially in view of the extreme difficulty of determining small concentrations of antioxidants in polyethylene.

According to Hildebrand and Scott,⁷ χ_1 at room temperature can be related to the solubility parameters δ_1 and δ_2 of solute and solvent, respectively, by the following approximate formula:

$$\chi_1 = V_1(\delta_1 - \delta_2)^2/RT. \quad (8)$$

From the results given in Figures 7, 8, and 9 and using the values of the molecular parameters given in Table IV, the values of χ_1 at 23°C (which are common to all the hydrocarbon solvents for a given antioxidant) are calculated to be 4.43 and 3.81 for Phenol A and Phenol B, respectively. Taking the value of δ_2 for hydrocarbons and polyethylene as 8.0, the solubility parameters calculated from these χ_1 values are 10.8 and 10.1, respectively, which are very reasonable in comparison with the solubility parameters of other similar moderately polar compounds.⁸

By comparing Figure 7 with Figure 8, we note that there is a large difference in the temperature coefficient of solubility between Phenol A and Phenol B. On the right-hand side of eq. (7), there are two terms that depend on temperature: $\Delta H_f/RT$ and χ_1 . As seen in Table IV, the heat of fusion ΔH_f of Phenol B is 16.4 kcal/mole, which is nearly twice the value of 8.66 kcal/mole for Phenol A. Such a large difference in ΔH_f is mainly a reflection of the difference in molecular size; actually, the heat of fusion per gram substance is lower for Phenol B than for Phenol A.

The term $\Delta H_f/RT$ constitutes between $\frac{1}{2}$ and $\frac{1}{3}$ of the total temperature dependence a/T (see eqs. (4) and (7)) of the solubility. The rest comes from the χ_1 term, which measures the excess free energy of mixing over the Flory-Huggins configurational entropy of mixing. Although the χ_1 term was originally considered to constitute only the excess enthalpy of mixing as is embodied in eq. (8), it is actually more appropriate to regard the χ_1 term as expressing the excess free energy of mixing, and only the temperature-

dependent part of χ_1 as the measure of excess enthalpy. By subtracting the quantity $\Delta H_t/RT$ from the total temperature dependence of solubility, a/T , we obtain the temperature-dependent part of χ_1 to be $1810/T$ and $5600/T$ for Phenol A and Phenol B, respectively. We immediately note that the ratio of the above quantities for the two compounds is nearly equal to the ratio of their molar volume. These analyses thus show that not only the absolute value of the solubility but also its temperature dependence is largely determined by the molecular size.

SUMMARY

A thermogravimetric technique was developed for the determination of a very small concentration of antioxidant additives in polyethylene. This technique was utilized to obtain the equilibrium solubility and diffusion coefficient of two antioxidants of hindered phenol type in branched polyethylene. In this method the amount of antioxidant which diffuses through a stack of polyethylene sheets is monitored, and the comparison of the concentration profile with the solution of the diffusion equation gives the values of the two quantities simultaneously.

The diffusion coefficients showed excellent agreement with values which were determined with antioxidants of similar chemical structure by a radio-tracer method. The solubilities of the two antioxidants were measured from 50° to 80°C and found to fall within at most a factor of 2 of the values predicted from the behavior of the antioxidants in several hydrocarbon solvents. The regular solution theory of liquid mixtures was found to be very useful in correlating the solubility data as a function of other thermodynamic properties of the solvent and solute molecules.

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Received August 20, 1973

Revised September 16, 1973