Solubility of Phenolic Antioxidants in Polyolefins

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Synopsis

The solubilities of six phenolic antioxidants in polypropylene and polyethylene were measured between 50°C and 100°C. Measurements were also made of their solubilities in a range of liquid alkanes. The measured solubilities at 70°C were consistent with regular solution theory and could be used to predict values to within one half of an order of magnitude. No simple correlation was found when regular solution theory was applied to predict the dependence of solubility on either temperature or the molar volume of the solvent. Hence, contrary to previous reports, the relative solubilities of antioxidants, measured at high temperatures or in alkane solvents, cannot be used to estimate their relative solubilities in polymers at room temperature.

INTRODUCTION

The solubility of small molecules in polymers is of interest for a number of practical applications. The permeability of packaging materials to gases, such as oxygen and carbon dioxide, is an important property, which is determined by the product of diffusion coefficient and solubility for the permeating gas. As a result the dependence of these parameters on temperature, polymer structure, and diffusant have been extensively studied.[1,2] Less is known about the solubility of involatile compounds in polymers, although there are many situations where this is of interest. For example, the extraction of additives by the contents of plastic packaging is a significant problem.[3] In the absence of swelling of the polymer by the contents, the exchange will principally be determined by the partition coefficient, the ratio of the solubility of an additive in the polymer to its solubility in the contacting material. This ratio is also important in the loss of drugs through plastic containers[4,5] and in the use of polymers as matrices for controlled drug release,[6,7] and its estimation requires knowledge of the solubility of the additive in both phases.

We have recently developed a model for the loss of additives from polymers, as part of an attempt to relate the results of accelerated ageing tests to antioxidant structure and properties.[8] According to our analysis, the loss of an additive is controlled either by the rate of its loss from the surface or by the rate of its migration through the bulk to reach the surface or by some combination of these parameters. The rate of loss of additive from a polymer surface can be predicted from the volatility of the pure additive and its solubility in the polymer, while the rate of migration of the additive to the surface to replace lost material is controlled by its diffusion coefficient. It follows that, for our model to have predictive value, we require data on the diffusion coefficient, solubility and volatility of the additives over the temperature range of interest, usually from ambient to 100°C.

Ideally it would be possible to predict the solubility of small, involatile mole-

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cules in polymers from measurements of their solubility in low-molecular-weight, homologous hydrocarbons, where it is relatively easy to make the solubility measurements. Several authors have suggested that this is possible, and it is quite common to quote the solubility of an additive in hydrocarbons as a measure of its compatibility with the polymer. Roe et al.[9] measured the solubility of two phenolic antioxidants in low-density polyethylene and in linear C_8, C_{16}, and C_{28} hydrocarbons. They suggested that regular solution theory could be applied predictively to these systems in that data for low molecular weight hydrocarbon analogues could be extrapolated to solubility in the polymer. Allara and White[10] reached similar conclusions about the solubility of copper carboxylates in hydrocarbons. Michaels et al.,[7] in a study of the solubility of steroids in polymers, found significant deviations from Hildebrand's theory of solubility but were able to make predictive correlations for a range of steroids.

In attempting to derive data for use with our model of additive loss from polymers, we have measured solubilities for a series of phenolic antioxidants in low-density polyethylene (LDPE), in polypropylene (PP), and in their low-molecular-weight analogues. We here present the results of these experiments and an attempt to analyze them in terms of regular solution theories, together with a critical evaluation of the possibility of predicting solubility in polymers from simpler measurements.

THEORY

The solubility of an additive in a polymer is determined by the free energy change associated with the transfer of the additive from its equilibrium state as a pure material into the polymer matrix. It is thus dependent on the physical state of the pure additive: The solubility of an amorphous additive is greater than that of the crystal form. It is now very well established[10,11] that soluble additives dissolve only in the amorphous phase of polyolefins so that measured solubilities require correction for crystallinity: There is no evidence for any morphological effect on solubility.

For a crystalline additive in contact with a polymer surface the solubility should be determined by the condition that the (negative) free energy of mixing of the liquid additive at the desired temperature is equal to the (positive) free energy required to convert crystalline additive to liquid at that temperature.[13] The free energy of fusion ΔG_f for a crystalline solid is given by

$$\Delta G_f = \Delta H_f - T\Delta S_f \tag{1}$$

and, since $\Delta S_f = \Delta H_f/T_m$, where T_m is the melting temperature of the additive, it follows that

$$\Delta G_f = \Delta H_f (1 - T/T_m) \tag{2}$$

The Flory–Huggins theory[14] of the mixing of liquids with polymers suggests that the partial molar free energy of mixing can be expressed as

$$\Delta G_m = RT[\ln \varphi_1 + (1 - V_1/V_2)\varphi_2 + \chi\varphi_2{}^2] \tag{3}$$

where φ_1, φ_2 are the volume fractions of additive and polymer respectively, V_1, V_2 are their molar volumes, and χ is the solvent solute interaction parameter. The first two terms in eq. (3) represent the geometric entropy of mixing while

the third term represents the nonideality of solution due to interaction between the polymer and the additive. Setting the sum of eqs. (2) and (3) to zero and putting $\varphi_2 \approx 1$ we obtain

$$-\ln \varphi_1 = \frac{\Delta H_f}{RT}\left(1 - \frac{T}{T_m}\right) + \left(1 - \frac{V_1}{V_2}\right) + \chi \qquad (4)$$

If it is assumed for the moment that χ is a constant for any given solvent-additive combination at all temperatures, then the first term of this equation gives the temperature dependence of the solubility of the additive. However, χ is a free energy term and may also be represented as

$$\chi = (\overline{\Delta H_1} - T\overline{\Delta S_1})/RT \qquad (5)$$

where $\overline{\Delta H_1}$ and $\overline{\Delta S_1}$ are the excess enthalpy and entropy of mixing, arising from interaction of solute and solvent. Alternatively this model can be extended by following Hildebrand and Scatchard[15] and expressing χ in terms of the solubility parameters of the solute and solvent (δ_1 and δ_2, respectively):

$$\chi = \frac{V_1}{RT}(\delta_1 - \delta_2)^2 \qquad (6)$$

These models can be tested in a number of ways:

(a) If χ is independent of the solvent molecular weight for a series of homologous solvents, a plot of the logarithm of solubility against $1/V_2$ should give a straight line of slope V_1, the molar volume of the solute. The intercept of this line at $1/V_2 = 0$ corresponds to the solubility of the additive in the homologous polymer.

(b) using solubility parameter theory, we can derive a value for $(\delta_1 - \delta_2)$ from each measurement of solubility. Using published solubility parameters of solvents, we can then derive a value for δ_1, the solubility parameter of the additive, which ought to be a constant, independent of the solvent for any given additive.

(c) If χ is temperature-independent, then the temperature dependence of additive solubility can be predicted from the heat of fusion of the additive, as contained in the first term on the right-hand side of eq. (4), and compared with experimental data. At temperatures above the melting point of the additive, the heat of fusion term in eq. (4) vanishes and the solubility should become temperature-independent if χ has no temperature dependence.
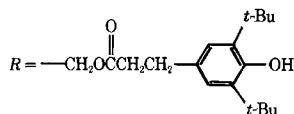
EXPERIMENTAL METHODS

The PP and LDPE used in our measurements were provided by I.C,I. Ltd., Plastics Division. The samples were free of additives, and the PP sample contained less than 3% of material soluble in boiling n-heptane. Both polymers were extruded without stabilizer to form thin films. The PP films were 110 μm thick, while the LDPE films were 220 μm thick.
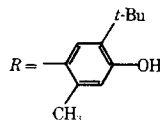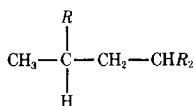
The additives, whose structures and properties are given in Tables I and II, respectively, were obtained commercially and used as received. Their melting points and heats of fusion were obtained by differential scanning calorimetry. Since the formation of metastable crystalline phases would affect the solubilities, a sample of each additive was recrystallized sequentially from chloroform and

TABLE I
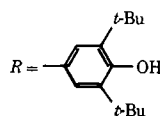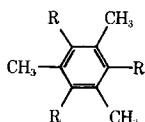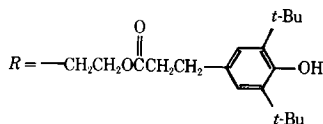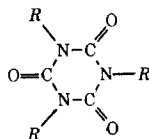Structures of Phenolic Antioxidants Used in Solubility Measurements

Irganox 1010
CR$_4$

$$R = -CH_2OCCH_2CH_2- \text{(3,5-di-}t\text{-Bu-4-OH phenyl)}$$

Topanol CA

$$CH_3-\underset{\underset{H}{|}}{\overset{\overset{R}{|}}{C}}-CH_2-CHR_2$$

$$R = \text{(2-}t\text{-Bu-4-OH-5-CH}_3\text{ phenyl)}$$

Ionox 330

$$CH_3-\text{(benzene ring, }R, CH_3, R, R, CH_3\text{ substituents)}-R$$

$$R = \text{(2,6-di-}t\text{-Bu-4-OH phenyl)}$$

Goodrite 3125

$$\text{(triazine-trione ring with N-R, N-R, N-R)}$$

$$R = -CH_2CH_2OCCH_2CH_2- \text{(3,5-di-}t\text{-Bu-4-OH phenyl)}$$

Plastanox 2246

$$t\text{-Bu}\overset{\overset{OH}{|}}{\bigcirc}-CH_2-\overset{\overset{OH}{|}}{\bigcirc}t\text{-Bu}$$
$$CH_3 \qquad CH_3$$
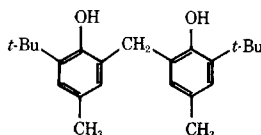
Santowhite Powder
R$_2$CHCH$_2$CH$_2$CH$_3$

$$R = \text{(2-}t\text{-Bu-4-OH-5-CH}_3\text{ phenyl)}$$
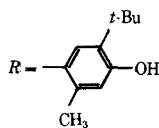
from hot or cold octane, while other samples were heated to 100°C for 72 h. The properties of these samples were then remeasured. After recrystallization from hot octane Ionox 330 showed a melting point 46°C lower than the as-received material. Topanol CA as-received contains 1 mol of toluene of crystallization per mole, which is released on heating, before melting occurs. On recrystallization from chloroform a phase with a lower heat of fusion and melting point was obtained, although this would not affect the present measurements. Many of the antioxidants were observed to melt to very viscous liquids which tended to form glasses rather than to crystallize on cooling.

The measurements of solubility in low-molecular-weight solvents were performed by shaking an excess of additive with the solvent in a water bath for up to 4 days and sampling the supernatant liquid after filtering through a 1–μm

TABLE II
Relevant Properties of Solvents and Solutes

A. Solvents			
Solvent	MW	Density at 70°C, g·cm^{-3}	δ, J$^{1/2}$cm$^{-3/2}$
Octane	114	0.662	14.43
Dodecane	170	0.712	15.34
Octadecane	218	0.748	15.56
Dimethylpentane	100	0.628	13.74
Pentamethylheptane	170	0.704	14.79
LDPE[a]		0.822	15.50
PP[a]		0.822	15.19

B. Solutes			
Antioxidant	MW	T_m, °C	ΔH_f, kJ·mol^{-1}
Topanol CA	544	183	41.8
Irganox 1010	1176	123	54.8
Goodrite 3125	1041	130	59.4
Ionox 330	774	245	46.0
Plastanox 2246	340	130	25.1
Santowhite P	382	212	40.1

[a] Amorphous phase.

filter. Equilibrium was usually reached in about 24 h. The resulting solution was diluted with chloroform to an appropriate concentration to allow determination of the additive content by uv spectroscopy. The phenolic peak at about 280 nm was used for the analysis, and the appropriate extinction coefficients were measured independently.

Measurements of the solubility of additives in the polymers were performed by the method of Feldshtein and Kuzminskii.[15] Alternating layers of additive and polymer film were clamped to form a "sandwich" which was held in an oven under a slow flow of nitrogen until equilibrium was established. Periodically films were removed, the surfaces were cleaned with cold ether, and the film was extracted in boiling chloroform for 2 h. UV spectroscopy of this chloroform solution was then used to determine the additive concentration. No changes in the uv spectrum with equilibration time, such as might accompany additive degradation, were seen. Some measurements were made in which three layers of polymer were placed between each layer of additive. The center layer reached the same final concentration as the outer two to within experimental error, demonstrating that the solid additive was not being ground into the film surface and that the surface washing procedure was effective.

Solubility parameters for low-molecular-weight solvents are easily determined with good precision and the values given in Table II are literature values for 25°C,[17] corrected to 70°C as described by Hildebrand.[15] (For consistency all solubility parameters quoted in this paper are expressed in J$^{1/2}$·cm$^{-3/2}$.) In contrast, values for polymers are more difficult to determine. There is general agreement that the solubility parameter for the amorphous phase of LDPE is around 16.2 at 25°C.[18] For the amorphous phase of semicrystalline PP, values of around 19.0 are conventionally quoted, although Ito and Guillet[19] have recently suggested a value of 15.7, based upon a gas-chromatographic estimation. The

chromatographic method generally yields reliable values for solubility parameters, and the value quoted for PP seems more consistent with what would be expected for a branched alkane polymer. Accordingly, we have chosen to use this new value in our calculations.

RESULTS

Figure 1 shows the uptake of Irganox 1010 by PP and by LDPE films at 60°C. It can be seen that equilibrium is reached in less than 2 weeks. Since this is a high-molecular-weight additive and so diffuses slowly, it can be assumed that true equilibrium was established in our measurements, which ran for 6–8 weeks.

Using an estimate of 3×10^{-11} cm²·s^{-1} for the diffusion coefficient of Irganox 1010 in polypropylene , one would predict the time to establish equilibrium in a 110-μm film to be 4 days at 70°C. For most additives, plots of log (solubility) against $1/T$ are good straight lines both for low-molecular-weight solvents and for polymers, and a representative selection of such plots is shown in Figure 2. The slopes of these plots are used to express the temperature dependence of solubility in terms of a heat of solution.

Table III presents solubility data for six phenolic antioxidants in terms of measured solubility at 70°C, extrapolated solubility at 25°C, and the heat of solution as determined from the temperature dependence of solubility. These solubility data have not been corrected for sample crystallinity. Table III also includes values of χ and δ calculated from regular solution theory using eqs. (4) and (6), with correction for sample crystallinity. There are few instances where different groups of workers have determined solubilities in the same system. Irganox 1010 has been studied by Frank and Frenzel,[20] Roe et al.,[9] and ourselves: these data are summarized in Figure 3. Our measured value of 0.4 wt % for the solubility of this additive in isotactic PP at 70°C compares well with the value of 1.5 wt % found by Frank and Frenzel when the numbers are corrected for crystallinity and for the lower solubility they find in molten isotactic PP compared to the lower molecular weight atactic material used for their solubility measurements. Our result for polyethylene (0.24 wt % at 70°C) is, however,
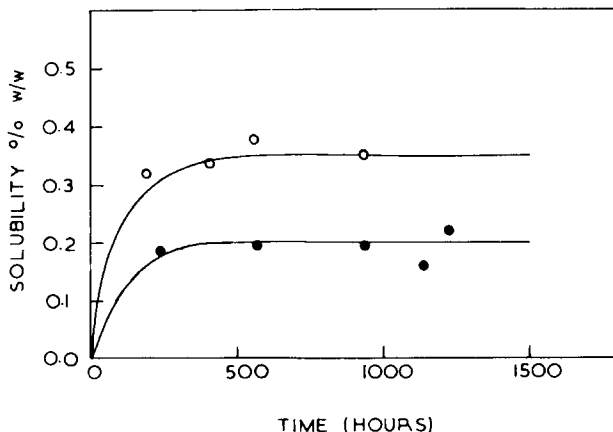

TIME (HOURS)

Fig. 1. Equilibration curves for diffusion of antioxidants into stacked polymer films at 60°C. (O) = Irganox 1010 into PP; (●) = Irganox 1010 into LDPE.
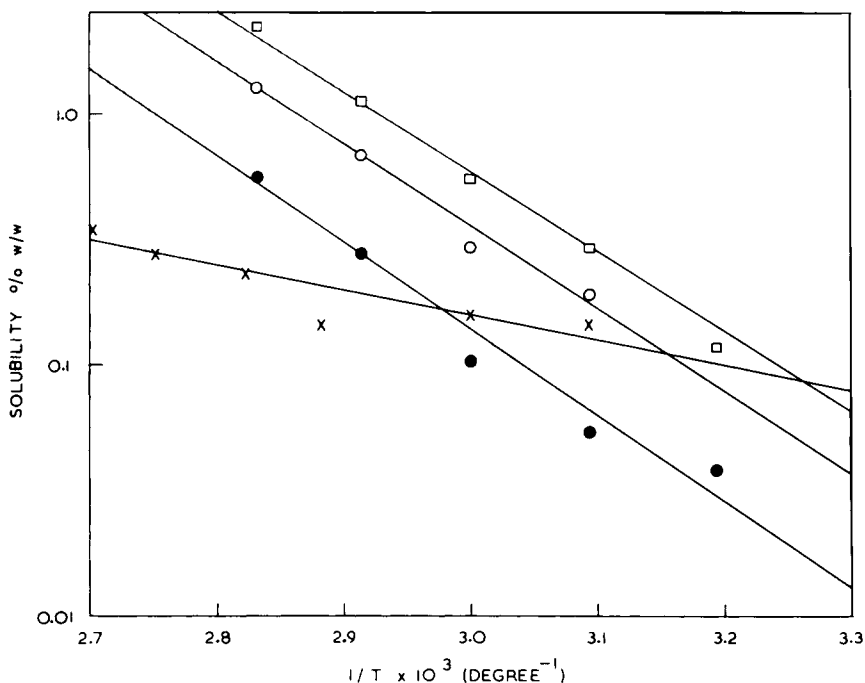
Fig. 2. Typical temperature dependence plots for additive solubility. All data are for Goodrite 3125. ($\square$) = n-octane; ($\circ$) = n-dodecane; ($\bullet$) = n-octadecane; (X) = LDPE.

much greater than that of Roe et al. (0.07 wt %). These latter authors also report solubilities in hydrocarbon liquids which are less than ours by a factor of 2–4. This discrepancy may be due to their use of thermogravimetric analysis for determining antioxidant concentrations in the polymer or to their use of dissolution with continuous heating for their solvent solubility measurements. With this rather significant exception, it seems that results of other workers for Irganox 1010 are comparable to ours. We have also shown elsewhere[21] that our results for other antioxidants are broadly comparable with those of others.

With reasonable confidence in the validity of our data we are able to test the regular solution theories in the ways outlined above.

a. Dependence of Solubility on Solvent Volume

In Figure 4 the logarithm of solubility is plotted against the reciprocal of the molar volume of the solvent for Irganox 1010 and Topanol CA in hydrocarbon solvents and in the polymers at 70°C, as required for a test of eq. (4). Roe et al. claimed that the slopes of such plots for their two antioxidants in LDPE corresponded to the molar volumes of the antioxidants as is predicted by equation 4 if χ is constant for the homogeneous series of solvents. We do not find this to be the case. The slopes of the lines for Irganox 1010 and Topanol CA in straight chain hydrocarbons are 315 cm^3 and 163 cm^3, respectively, compared to molar volumes of about 1200 cm^3 and 550 cm^3. From this we conclude that χ cannot be considered to be constant within a homologous series of solvents. This fact is also discernable from the values given in Table III. χ decreases consistently with increasing molecular weight of the solvent.

TABLE III
Solubilities and Derived Parameters for Antioxidants

Additive	Solvent	Solubility 70°C, % w/w	χ	δ_1, J$^{1/2}$·cm$^{-3/2}$	Solubility 25°C, % w/w	ΔH_s, kJ·mol^{-1}
Topanol CA	Octane	0.73	4.1	18.8	0.30	20 ± 2
	Dodecane	0.60	3.2	19.2	0.22	19 ± 2
	Octadecane	0.39	3.1	19.4	0.14	19 ± 2
	LDPE	0.12	1.5	18.2	0.009	50 ± 1
	Dimethylpentane	0.36	5.1	18.6	0.14	19 ± 2
	Pentamethylheptane	0.28	4.0	19.0	0.083	23 ± 1
	PP	0.20	1.1	18.6	0.002	80 ± 6
Irganox 1010	Octane	3.84	7.6	18.6	0.076	77 ± 6
	Dodecane	2.04	6.0	19.0	0.054	76 ± 17
	Octadecane	1.21	5.5	19.0	0.034	67 ± 2
	LDPE	0.24	1.9	17.6	0.020	39 ± 4
	Dimethylpentane	2.77	8.6	18.0	0.032	85 ± 2
	Pentamethylheptane	1.67	6.2	18.4	0.24	37 ± 3
	PP	0.40	1.5	17.0	0.15	32 ± 6

|						
Goodrite 3125	Octane	1.12	7.4	18.8	0.032	68 ± 2
	Dodecane	0.68	6.0	19.2	0.021	55 ± 5
	Octadecane	0.27	6.0	19.4	0.007	64 ± 7
	Dimethylpentane	0.76	8.4	18.4	0.007	88 ± 4
	Pentamethylheptane	0.89	5.7	18.6	0.014	83 ± 8
	PP	0.19	1.7	17.2	0.071	18 ± 5
Ionox 330	Octane	5.28	1.9	17.0	0.73	35 ± 1
	Dodecane	2.62	1.0	17.2	0.33	39 ± 2
	Octadecane	1.37	1.0	17.4	0.12	44 ± 3
	Dimethylpentane	4.68	2.4	16.6	0.68	36 ± 1
	Pentamethylheptane	2.40	1.1	16.6	0.27	44 ± 4
	PP	0.11	0	15.1	0.004	63 ± 8
Plastanox 2246	Octane	34.92	2.2	18.6	4.36	42 ± 6
	Dodecane	18.00	1.6	18.8	3.20	38 ± 1
	Octadecane	12.34	1.6	19.0	2.15	41 ± 4
	PP	4.3	0.5	17.2	1.17	27 ± 4
Santowhite P	Octane	0.68	2.6	18.6	0.13	31 ± 3
	Dodecane	0.47	2.2	19.2	0.12	26 ± 2
	Octadecane	0.33	2.2	19.4	0.10	21 ± 1
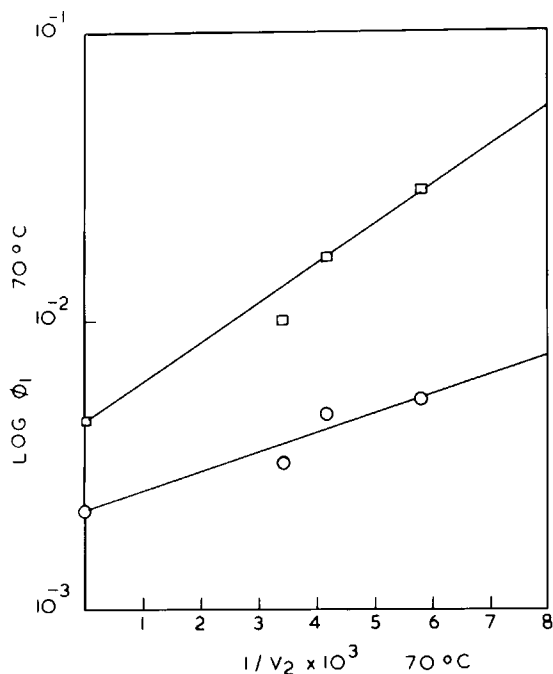
Fig. 3. Summarized data for temperature dependence of the solubility of Irganox 1010, corrected for polymer crystallinity. (+) = our data for LDPE; (□) = our data for PP; (●) = data of Frank and Frenzel for atactic PP; (O) = data of Frank and Frenzel for Isotactic PP; (X) = data of Roe et al. for LDPE.

b. Solubility Parameters from Solubility Data

Turning our attention to Hildebrand's formulation of regular solution theory, the values of solubility parameter difference $(\delta_1 - \delta_2)$ can be determined from the available data, and hence values of the solubility parameter of the additive can be computed, knowing the solubility parameters of the solvents $(\delta_2$, Table II). On this basis, using data for the low-molecular-weight solvents, we find that each additive gives a solubility parameter constant to ±0.4, as shown in Table III. This corresponds to an uncertainty of plus or minus half an order of magnitude in solubility. However, the values derived from the polymer solubility data deviate significantly from those obtained from solvent solubilities. This could be resolved by altering the polymer solubility parameters, for instance, an increase of about 1.4 for polypropylene, but such juggling hardly seems justified on the basis of data on a single class of solutes. Solubility parameters for the antioxidants calculated by Small's method[22] are in the region of 17.4–19.4 and vary largely due to uncertainties in crystal density. There is no correlation between the values calculated and those given in Table III.

c. Temperature Dependence of Solubility

The variations of solubility with temperature expressed as a heat of solution are given in Table III. Our data for Irganox 1010 show slight curvature around 100°C as seen in Figure 3. However, the data of Frank and Frenzel[19] suggest that this change in slope is not maintained, but rather that the same heat of so-
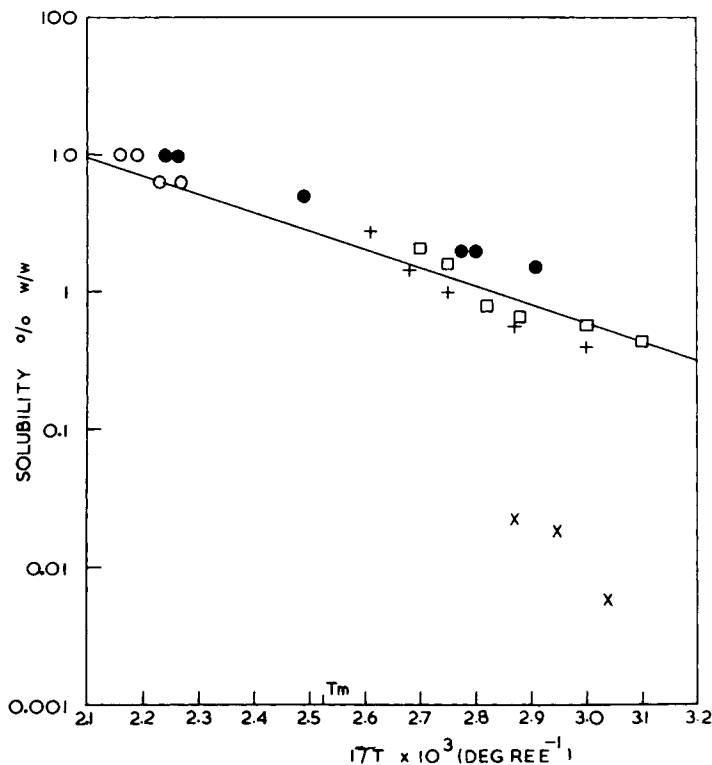
Fig. 4. Dependence of solubility on the molar volume of the solvent. All data are for linear hydrocarbons and LDPE. ($\square$) = Irganox 1010; ($\odot$) = Topanol CA.

lution governs solubility in both the liquid and solid polymers and for both liquid and solid additives. The other antioxidants show no significant curvature in log (solubility) versus $1/T$ plots.

The temperature dependence of solubility can be derived from eq. (4) as

$$- \frac{\partial \ln\varphi_1}{\partial(1/T)} = \frac{\Delta H_f}{R} + \frac{\partial \chi_1}{\partial(1/T)} \tag{7}$$

If χ is independent of temperature, then the temperature dependence of solubility expressed as a heat of solution $[-R\partial\ln\varphi_1/\partial(1/T)]$ should be equal to the molar heat of fusion of the additive. That this is not the case can be readily seen by comparing Tables II and III. Deviations of up to ±40 kJ·mol^{-1} are observed, and even an amorphous additive such as molten Irganox 1010 shows substantial variation in solubility with temperature. Using eq. (5) it is possible to obtain values for the enthalpy and entropy of interaction, $\overline{\Delta H}_1$ and $\overline{\Delta S}_1$, but these cannot be readily interpreted. If we formulate χ in terms of solubility parameters then we obtain, using eq. (6),

$$- \frac{\partial \ln\varphi_1}{\partial(1/T)} = \frac{\Delta H_f}{R} + \frac{V_1(\delta_1 - \delta_2)^2}{R} - \frac{T(\delta_1 - \delta_2)^2}{R} \frac{\partial V_1}{\partial T}$$
$$- \frac{2TV_1(\delta_1 - \delta_2)}{R} \frac{\partial(\delta_1 - \delta_2)}{dT} \tag{8}$$

There is no reason to think that the third and fourth terms on the right-hand

side of eq. (8) can be ignored.   Indeed the second term can only be positive, while the difference $(-\partial\ln\varphi_1/\partial(1/T) - \Delta H_F/R)$ can be either positive or negative.   The second term can be estimated reliably, while the third and fourth cannot.   Thus regular solution theory offers little guidance on the temperature dependence of solubility.

DISCUSSION

From the foregoing it is clear that the solubility parameter theory is of use when applied to antioxidant solubility in hydrocarbon solvents but is very poor when applied to their solubility in polymers.   There seems to be no experimental justification for assuming that either χ or its temperature dependence are constant for a series of homologous solvents and for the corresponding polymer. This is a significant point since this assumption is central to attempts to use additive solubilities in solvents to predict their solubilities in polymers.   In particular, if data for solvents are extrapolated using eq. (4), we find that predicted solubilities in polymers are one or two orders of magnitude lower than experimentally determined values.

This significant difference in behavior between the polymers and the solvents is perhaps not surprising in view of the much greater packing density of the liquid polymers.   For the purposes of predicting solubility, it would seem that a reliable value for the solubility of a phenolic antioxidant at 70°C could be obtained by measuring its solubility in octane at this temperature, obtaining a solubility product for the antioxidant and hence calculating the solubility in the polymer, using solubility parameters of 19.4 and 16.4 for PP and LDPE respectively. Solubilities extrapolated to 25°C are not amenable even to this simple treatment as the temperature coefficients of solubility are so variable.

Polar impurities may also be important in determining the solubility of antioxidants in polymers, particularly in view of the difficulty in producing unstabilized films without degradation of the polymer.   Allara and White[10] have found that the apparent solubility of copper carboxylates in LDPE increases with the degree of oxidation of the film.   It should be noted that it is generally impossible to process unstabilized polymer without degradation, so that there are real problems in trying to do controlled experiments on this effect.   Addition of small amounts of methyl nonyl ketone or lauric acid to n-dodecane produced no enhancement of additive solubility so this effect, if it exists, may be important only in the denser, polymeric systems.

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