

Diffusion and Solubility of Hydroxy Compounds in Polyolefines

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Synopsis

The diffusion and relative solubility coefficients of some alcohols, phenols, and antioxidants have been measured by a permeation method for LDPE at room temperature. The diffusion coefficients of the hydroxy compounds are compared with those of the alkanes. The diffusion coefficients of the alkanes mark out upper limiting values which are not exceeded by the hydroxy compounds of comparable molecular weight.

INTRODUCTION

The importance of aromatic hydroxy compounds (antioxidants) as protective substances in polymers to avoid oxidation and decomposition reactions by molecular oxygen is well known. The reaction, diffusion, and solubility behavior of these compounds are interesting for polymer chemists especially in view of molecular weight and molecular structure dependence of these compounds. Food chemists and packaging technologists are also interested in diffusion and solubility data of these compounds because antioxidants are able to migrate from the package (polymer) to the packed good (food, medical supplies) and therefore can contaminate the packed good in an undesired manner.

Though other authors^{1,2} have investigated the diffusion and solubility of some phenolic antioxidants some years ago, a further investigation seemed to be interesting and useful because nowadays the analytical methods (capillary gas chromatography, mass spectrometry in SIM-mode) are greatly improved. Hence, both a radioactive labeling of antioxidants of large molecular weight (e.g., for molecular weights larger than 500) to lower the detection limit by applying a radioanalytical determination method or the realization of diffusion measurements at increased temperatures to raise the diffusion rate are not always necessary. Errors and faults resulting from radioactive labeling (measurement of decomposition products) or by extrapolation of data from high temperature to room temperature are excluded.

As hydroxy derivatives we have chosen some low-molecular alcohols and phenols to study their diffusion and solubility behavior in comparison to *n*-alkanes and some higher molecular antioxidants which are used in practice. As polyolefine we have chosen LDPE.

EXPERIMENTAL

The permeation method has been carried out using the method briefly described in the foregoing paper³ and in detail elsewhere.⁴ Simultaneous permeation of more than one compound was measured out of a diluted ethanolic solution (0.1-0.5 wt%) through the polymer into ethanol.

The alcohols and alkyl-substituted phenols, purchased from Fluka and Ega, are of the highest available purity, and used without further purification.

The antioxidants 3,5-di-*t*-butyl-4-hydroxy-benzoic acid-(2,4-di-*t*-butylphenyl)-ester (tinuvin 120), 2-(2-hydroxy-3-*t*-butyl-5-methylphenyl)-5-chlorobenzotriazol (tinuvin 326), 1,1,3-tris(2-methyl-4-hydroxy-5-butylphenyl)butane (topanol) were donated by a chemical company.

The polymer film which had a mean thickness of 50 or 100 μm was LDH 1018 (Hoechst AG) with a specific density of 0.918.

The alcohols and alkylated phenols have been determined by capillary gas chromatography and the antioxidants by high-performance liquid chromatography with an electrochemical detector.⁵ The columns for HPLC analysis have been products of Machery-Nagel (Nucleosil 10-C-18) and Merck (LiChrosorb RP-18). The used solvents have been of HPLC quality.

RESULTS AND DISCUSSION

Our main interest has been focused on the comparison of the alkane diffusion coefficients with those of the hydroxy derivatives. In contrast to our alkane measurements we have not determined the temperature dependence of the diffusion and solubility.

The results of the measurement of the diffusion and relative solubility constants of the *n*-alkanes have shown that the diffusion process in solution which can be interpreted in the Einstein or Eyring model resembles to a certain degree that in the polymer whereby the diffusion coefficients in a liquid are correlative with the cube roots of the molar volumes (Einstein model) or the logarithms of the diffusion coefficients with the heats of vaporization which are proportional to their boiling temperatures (Eyring model) (for references and more details see the foregoing paper).

Table I shows some diffusion and relative solubility constants of straight

TABLE I
Diffusion, Relative Solubility, and Relative Permeation Constants of Some Alcohols
in LDPE at 23°C, Compounds Dissolved in Ethanol

Compound		$D \cdot 10^{10}$ (cm^2/s)	S_r	$P_r \cdot 10^{10}$ (cm^2/s)
Name	Structure			
Methanol	CH_3OH	480		
Heptanol	$\text{CH}_3(\text{CH}_2)_5\text{CH}_2\text{OH}$	55	0.0047	0.26
Nonanol	$\text{CH}_3(\text{CH}_2)_7\text{CH}_2\text{OH}$	40		
Dodecanol	$\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{OH}$	11	0.021	0.23
Tetradecanol	$\text{CH}_3(\text{CH}_2)_{12}\text{CH}_2\text{OH}$	8.2	0.029	0.23
Hexadecanol	$\text{CH}_3(\text{CH}_2)_{14}\text{CH}_2\text{OH}$	6.4	0.033	0.21
Octadecanol	$\text{CH}_3(\text{CH}_2)_{16}\text{CH}_2\text{OH}$	4.8	0.053	0.25

chain primary alcohols. For the definition of the relative solubility data see the foregoing paper.

The diffusion coefficient of methanol has been calculated by the time lag and in all other cases by the experimentally determined permeation and solubility constants. The constant of nonanol has been determined out of aqueous solution.

In the case of the straight-chain alcohols we are able to compare the diffusion in the polymer with that in solution. Interpreting the data in the meaning of the Eyring model we see that the diffusion coefficients in solution (benzene as solvent, data taken from Rossi and co-workers)⁶ and those in the polymer are correlative with the heats of vaporization (Fig. 1). In the case of hexadecanol and octadecanol, the boiling constants have been extrapolated from literature⁷ at reduced pressure to normal pressure and show a little uncertainty as indicated in the plots. Just these two alcohols show a deviation from linearity in the case of the diffusion in solution. Such a deviation has not been observed in the case of *n*-alkanes (foregoing paper). Apart from this, the two correlations are satisfactory but not as good as the alkane correlations.

Figure 2 shows a plot of the logarithms of the relative solubility constants (partition coefficients, alcohols partitioned between ethanol and LDPE) versus the carbon number. As in the case of the *n*-alkanes, we get a straight line, which indicates that the partial molar free energy resulting by partitioning the alcohols between ethanol and LDPE is a linear function of the lipophilic CH₂-units.

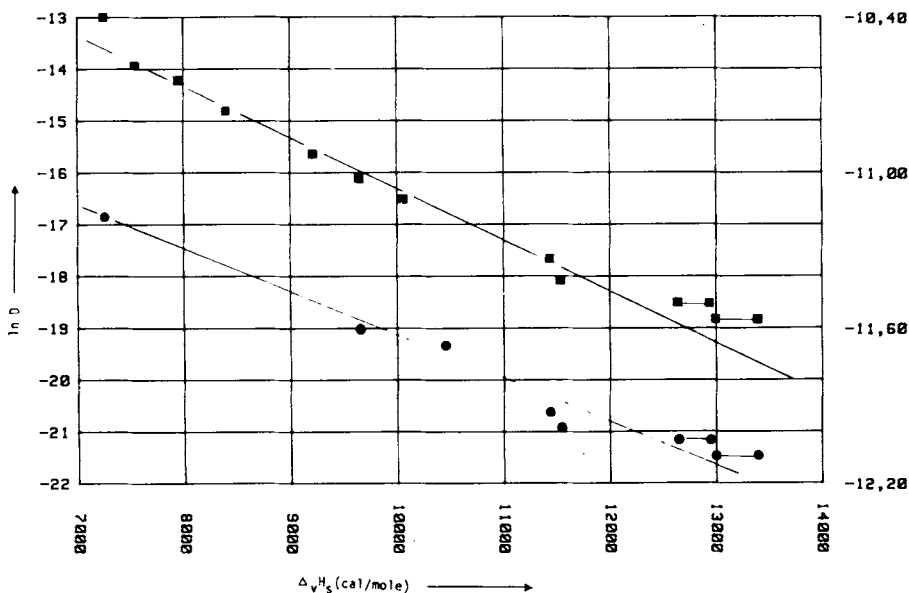


Fig. 1. Diffusion coefficients D (cm^2/s) of alcohols in relation to their heats of vaporization; upper curve (■) diffusion coefficients in benzene, right ordinate, alcohols with 1, 2, 3, 4, 6, 7, 8, 12, 14, 16, and 18 carbon atoms (in the turn from left to right); lower curve (●) diffusion coefficients in LDPE, left ordinate, alcohols with 1, 7, 9, 12, 14, 16, and 18 carbon atoms (in the turn from left to right).

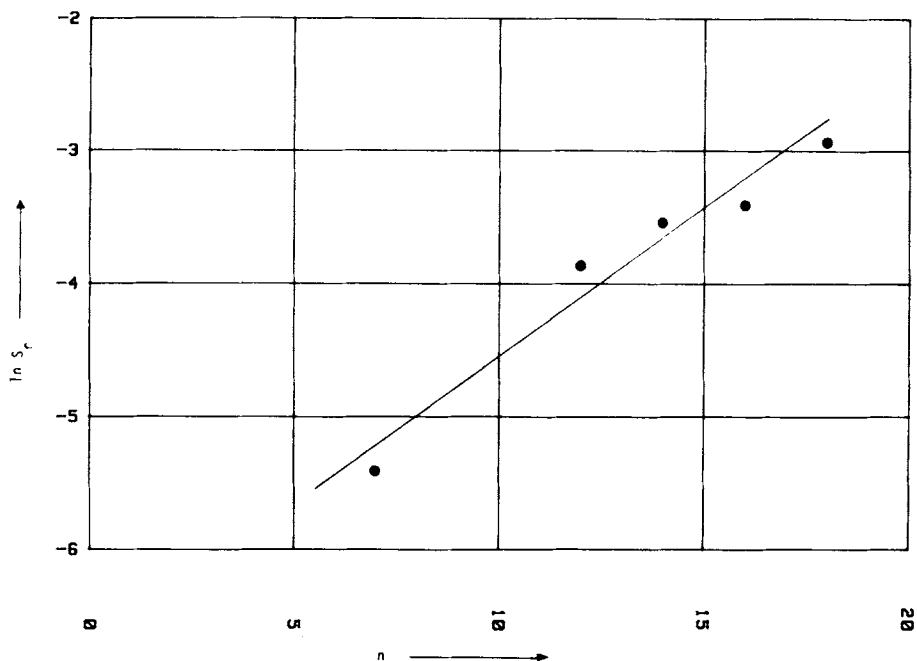


Fig. 2. Relative solubility constants S_r of the alcohols for the system LDPE/ethanol, alcohols dissolved in ethanol, as function of the carbon number n .

Table II shows the diffusion, relative solubility, and relative permeation constants of some phenolic antioxidants. The phenols which we have measured do not represent a homologue series as the straight-chain alkanes or primary alcohols. We have investigated *ortho* and *para* substituted and both partially and totally shielded phenols. It is clear that in such a case the situation is not so simple and the dependence of the diffusion and solubility constants from molecular-specific properties is more complex. But

TABLE II
Diffusion, Relative Solubility, and Relative Permeation Constants of Phenols and Antioxidants in LDPE at 23°C, Compounds Dissolved in Ethanol

Compound Name	$D \cdot 10^{10}$ (cm ² /s)	S_r	$P_r \cdot 10^{12}$ (cm ² /s)
Phenol	45	0.0026	12
<i>p</i> -Cresol	23	0.0056	13
2,4,6-Trimethylphenol	23	0.019	44
2,3,5,6-Tetramethylphenol	16	0.03	48
2,4-Di- <i>t</i> -butylphenol	1.2	0.016	1.9
2,6-Di- <i>t</i> -butylphenol	9.8	0.13	130
2,6-Di- <i>t</i> -butyl-4-methylphenol	6.6	0.19	125
3,5-Di- <i>t</i> -butyl-4-hydroxy-benzoic acid-(2,4-di- <i>t</i> -butyl-phenyl)-ester (Tinuvin 120)	0.18	0.045	0.81
2-(2-hydroxy-3- <i>t</i> -butyl-5-methylphenyl)-5-chlorobenzotriazol (Tinuvin 326)	2.0	0.71	140
1,1,3-Tris(2-methyl-4-hydroxy-5- <i>t</i> -butylphenyl)butane (Topanol)	0.054	0.00031	0.0017

comparing the diffusion coefficients of phenol with methyl-substituted phenols we see that the diffusion rates of the phenols decrease if the hydrogen atoms are replaced by methyl groups step by step.

The introduction of alkyl substituents in both the *ortho* position to the OH function leads to a strong shielding of the OH groups, whereby the hydrogen bond between two phenols, the intermolecular interaction, is diminished. This shielding is physically observable, for example in a reduction of the boiling or the melting points (mp = 34-37°C for 2,6-di-*t*-butylphenol, 54-56°C for 2,4-di-*t*-butylphenol). Accordingly, this shielding should lead to a larger diffusion coefficient because of the proportionality between the heat of vaporization and the activation energy in the meaning of the Eyring model. A comparison of the diffusion coefficients of 2,4-di-*t*-butylphenol with that of 2,6-di-*t*-butylphenol shows that 2,6-di-*t*-butylphenol has a diffusion coefficient eight times larger than that of 2,4-di-*t*-butylphenol. The effect of the shielding, whereby the acidity of the OH function is diminished, is also visible in the relative solubility constants. Here the shielded phenol is about the factor eight more soluble in the polyolefine than the partially shielded phenol. Because the permeation constant is the product of the diffusion and solubility constant, the factor for the permeation is 64.

There is no clear dependence of the diffusion coefficients of the different phenols with their heats of vaporization. This results from the nonhomolog series the phenols represent. Furthermore, since there is a lack of thermodynamic data for the higher phenols (heats of vaporization) we only show diagrams where the diffusion coefficients are plotted versus their molecular weights. Figure 3 shows such a diagram with the diffusion coefficients of some phenols in comparison with those of the straight-chain alkanes and alcohols. The diffusion coefficients of those alkanes which could not be

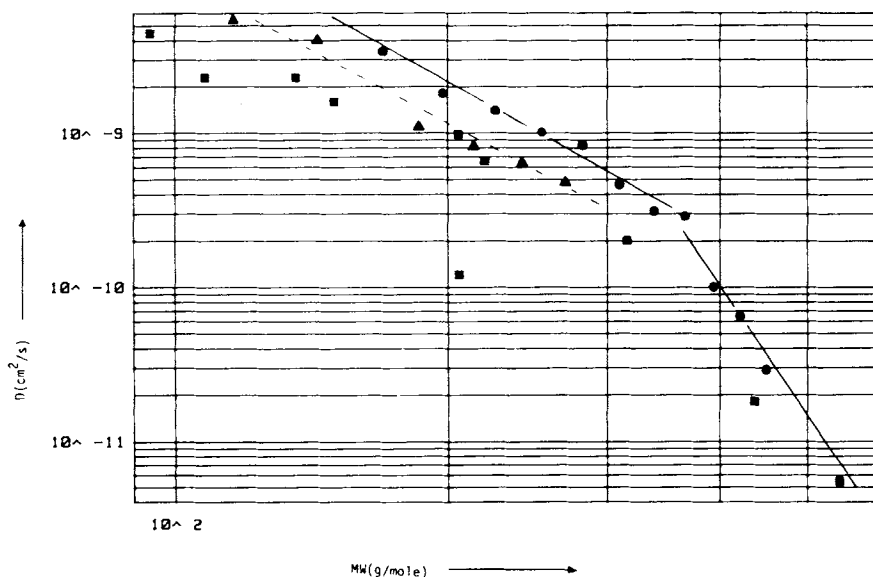
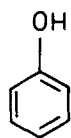
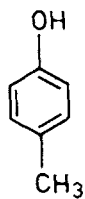


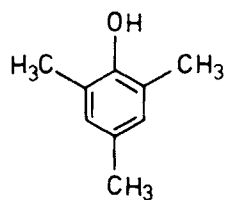
Fig. 3. Comparison of the diffusion coefficients of the alkanes (●), (—) with those of the alcohols (▲), (- - -) and phenols (■) as function of their molecular weights.



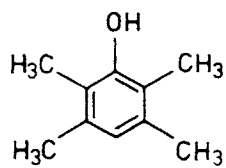
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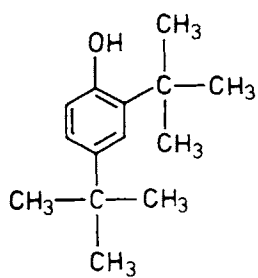
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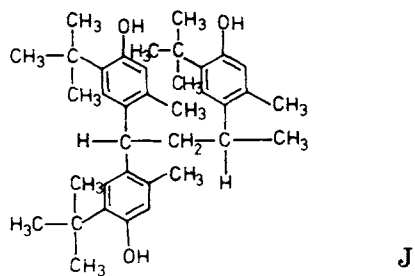
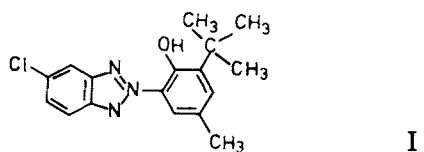
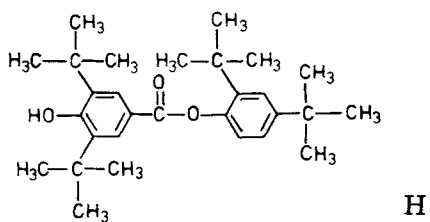
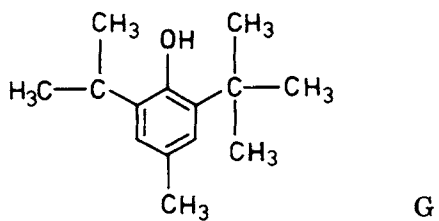
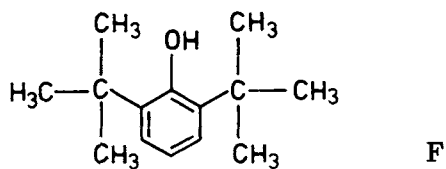
C



D



E



measured out of ethanolic solution on account of their low solubility have been extrapolated from constants of Table IV of the foregoing paper.³ All the measured alcohols and phenols show diffusion coefficients being always lower than those of the alkanes having the same molecular weight. By increasing the molecular weight of the phenols, their diffusion coefficients approach very closely those of the alkanes, because the influence of the OH function is diminished by increase of the carbon and hydrogen atoms. Therefore, the diffusion coefficients of the *n*-alkanes in the polyolefines mark out an upper limiting value. This means that all compounds with OH functions have diffusion coefficients lower, or at most, the same as those of the corresponding (hypothetical) *n*-alkanes. We have indications that this is true for a variety of other functions.

In the literature we find two papers with data of antioxidants which are comparable with our data. Roe, Bair, and Gieniewski¹ have determined the diffusion coefficients in LDPE for two phenols at 60° to 80°C with the aid of a thermogravimetric method. The extrapolation of their diffusion coefficients to 23°C leads to a value of $1.2 \cdot 10^{-9}$ cm²/s for 4,4-thiobis(3-methyl-6-*t*-butylphenol) with molecular weight 358 and $2.6 \cdot 10^{-10}$ cm²/s for tetrakis(methylen-3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionate)-methane with molecular weight 1176. These constants seem to be too large by about one to two powers of ten compared with the coefficients of our phenols. An explanation for this may be that the extrapolation from the measured temperature region of 60–80°C is too inaccurate.

Jackson, Oldland, and Pajaczkowsky² have determined the diffusion coefficient for 1,1,3-tris(2-methyl-4-hydroxy-5-*t*-butylphenyl)butane for LDPE at 100, 78, and 56°C with the aid of a radio tracer method. One calculates a diffusion coefficient of $6.0 \cdot 10^{-10}$ cm²/s at 23°C from their values (activation energy and the Arrhenius pre-exponential factor). We find a value of $5.4 \cdot 10^{-12}$ cm²/s for the same antioxidant with molecular weight 544. The value found by Jackson and co-workers is too large compared with our value, especially if comparing with the diffusion coefficients of the *n*-alkanes of Figure 3. The large value may result from experimental errors; the authors applied a hexane solution of polyisobutylene and radioactive-labeled 1,1,3-tris(2-methyl-4-hydroxy-5-*t*-butylphenyl)butane which they brought into contact with the polymer sheet. After removing the hexane the LDPE sheet was coated with the resulting polyisobutylene layer with the now incorporated antioxidant. Then the authors observed the diffusion of the antioxidant out from the polyisobutylene layer into the LDPE. It could be possible that the hexane has been carried to the LDPE so that a possible swelling of the polymer combined with an irreversible alteration of the morphology would explain the too large value.

The same authors have also determined the diffusion constants of octadecane and the according activation energy. They find a value of 12.4 kcal/mole for octadecane and 12.2 kcal/mole for 1,1,3-tris(2-methyl-4-hydroxy-5-*t*-butylphenyl)butane. Values of about 12 kcal/mole were found too for a variety of other substances. Jackson and co-workers concluded from this that the size of the molecule has no influence on the diffusion rate. These results are also contradictory to our experience. We have found activation energies of 13.7, 15.7, and 25.7 kcal/mole for dodecane, octadecane, and

dotriacontane, respectively, even for the diffusion in hexane swollen LDPE (foregoing paper). In unswollen LDPE the activation energy grows with increasing molecular weight.

The relative solubility constants of the phenols grow with increasing substitution. But we have to distinguish between shielded and unshielded phenols. The shielded phenols are more soluble in the polyolefine due to their lower acidity.

We want to state here that it is better and easier to operate with relative solubility and relative permeation constants though these constants are solvent dependent. The absolute pressure-related magnitudes are difficult to measure and are almost useless; these magnitudes are only useful if the pressure relations of the permeate (polymer/air or polymer/solvent system) are known; but this is seldom the case.

CONCLUSION

The diffusion and relative solubility constants of hydroxy components in polyolefines have been measured by a permeation method. The trend of the diffusion of the alcohols is explainable by Eyring's rate transition theory. As in the case of the alkanes there exists a relation between the logarithm of the diffusion coefficients and their heats of vaporization. The phenols do not show such a clear relation, but the diffusion coefficients fall down with increasing molecular weight of the diffusing species. The shielded phenols have diffusion coefficients which are greater than those of the unshielded phenols. This is consistent with the Eyring model. The diffusion coefficients of the alcohols and phenols are lower than those of the comparable alkanes. Therefore the alkanes mark out an upper limiting value which cannot be exceeded by the hydroxy compounds. This is an interesting fact, because this allows one, if the diffusion coefficients of the alkanes are known, to estimate a maximum diffusion coefficient.

The logarithms of the relative solubility constants of the alcohols are linear functions of their carbon numbers.

The diffusion constants measured in this study are applicable to foods which are not able to swell the polymer, such as aqueous, alcoholic, and acidic food.

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