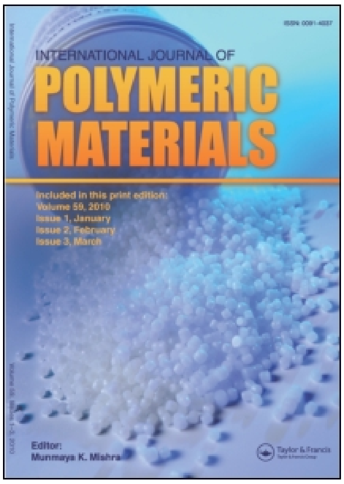

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Effect of Heptadecane on Sorption of 2,6-di-Tert-butyl-4-Methylphenol by Polyethylene

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The sorption of vapors of 2,6-di-tert-butyl-4-methylphenol (DTP) by HDPE containing different concentrations of heptadecane has been studied using the ultraviolet spectrometry method. The isotherms of DTPh sorption at 100–200°C are presented by the Langmuir equation. The concentration of sorption of DTPh has no dependence on temperature, but depends on the concentration of heptadecane in a polymer. The heats of dissolution of DTPh in polyethylene have been determined.

KEY WORDS Sorption, polyethylene

INTRODUCTION

It has been shown earlier in the study of sorption of low molecular weight compounds in polymers that the dependence of an equilibrium concentration of an additive in a polymer $[A]_p$ on its concentration in a surrounding medium $[A]_m$ can be described by a law analogous to the Langmuir equation:

$$[A]_p = a[A]_m \cdot (1 + b[A]_m)^{-1} \tag{1}$$

where a and b are the constants: the a/b ratio corresponds to the limiting concentration of A in a polymer.

Such dependence infers an existence of certain limited concentration of sorption centers in a polymer and, therefore, the process of dissolving a compound in the polymer may be considered as the process of filling these centers.

The nature of sorption centers may be different. The polymer polar groups interacting with an additive (for example, due to the formation of hydrogen bonds), as well as the regions with a lesser density of a polymer substance (the elements of free volume) in the polymer may be regarded as such centers. The latter have either a relaxation,[1] or a topological[2] nature.

The first who paid attention to the existence of the specific features of dissolution of low molecular weight compounds in polymers were Barrer, Barrie and Slater,[3] in studying the sorption and diffusion of lower hydrocarbons in ethylcellulose at a temperature below the polymer glass-transition temperature. They showed that this medium, regarding the sorption properties, differs considerably from elastomers. The sorption isotherms obtained by the authors of Reference 3 were presented by the Langmuir equation; the same authors noted negative values of enthalpy and entropy of dissolution. The authors explained this situation by the peculiarities of packing of rigid cellulose macromolecules which results in the formation of microcavities capable of concentrating sorbate molecules without additional deformation of the polymer segments.

Later, this model, called the dual-mode sorption model, was developed in the works of Michaels and Vieth,[4] who used it for the quantitative description of sorption and gas transfer in glassy polymers.

In accordance with the dual-mode sorption model, the total concentration of the compound dissolved in a polymer is equal to the sum of concentrations of the truly dissolved compound obeying Henry's law and of that sorbed in compliance with Langmuir's law:

$$[A]_p = \gamma[A]_m + a[A]_m \cdot (1 + b[A]_m)^{-1} \tag{2}$$

where γ is the coefficient of the distribution between the polymer and surrounding medium; $\gamma = [A]/[A]_m$; and $[A]$ is the concentration of the truly dissolved compound.

In compliance with Reference 1, these centers are microcavities and exist in a polymer at temperatures below the polymer glass-transition temperature, whereupon their concentration $[Z]$ decreases as the temperature increases. In the vicinity of the glass-transition temperature the sorption law is violated.

However, as the experimental data indicate,[2] alongside such nonrelaxed polymer areas, the more stable topological formations may exist in this polymer. The short-range order violations in the arrangement of macromolecules—ends, loops, overlaps and bendings, which are relatively stable due to the large length of macromolecules and can exist for a long time even at the temperatures above the polymer melting temperature—may be the basis for such formations.

It has been shown in References 5–7, that the sorption of additives of molecular mass 200–1000 by polyolefins, when introducing them into a polymer from the solutions in low molecular weight solvents or from a gas phase, is governed by a law, (2), whereupon, the Langmuir sorption limit a/b remains constant within a wide range of temperatures, even above the polymer melting point, while the value $[A]_m$ may be ignored. Close to the temperatures corresponding to the phase transitions, the value $a/b = [Z]$ may change jumpwise, however, outside of these temperature ranges this value remains constant.[6] The character of sorption isotherms can change and, correspondingly, the Langmuir law of sorption can be violated at large concentrations of low molecular weight compounds dissolved in a polymer,[7] which is explained by the plasticization of the polymer with an additive.

Whatever the nature of the sorption centers, the process of dissolving a low molecular weight compound A in the polymer may be presented in the form of a reversible interaction of the truly dissolved compound A with the sorption centers Z:

$$A + Z \underset{}{\overset{K_a}{\rightleftharpoons}} AZ. \tag{3}$$

Then

$$K_a = \frac{[AZ]}{[A]([Z] - [AZ])}.$$

Assuming that $[A] << [AZ]$, we can obtain

$$[A]_p = \frac{K_a\gamma[A]_m \cdot [Z]}{1 + K_a\gamma[A]_m}, \tag{4}$$

or

$$1/[A]_p = 1/[A]_m \cdot \frac{1}{K_a\gamma[Z]} + \frac{1}{[Z]}.$$

Should a second compound B being sorbed by the same centers as A be present in the polymer alongside compound A, a competition for the sorption centers is possible and compound B will replace A from the sorption centers

$$AZ + B \rightleftharpoons A + BZ. \tag{5}$$

In this case, the presence of B should result in a decrease of solubility of A in the polymer

$$[A]_p = \frac{([Z] - [B]_p)\gamma[A]_m K_a}{1 + K_a\gamma[A]_m}. \tag{6}$$

However, substance B can also rearrange the sorption centers or, dissolving outside of them, facilitate their subsequent rearrangement. Such a process can be formally presented as follows:

$$B + Z \rightarrow BZ \rightarrow B + Z^*. \tag{7}$$

As a result, the concentration of the sorption centers accessible for A can either increase or decrease.

In the present work, the authors studied the sorption of 2,6-di-tert-butyl-4-methylphenol (DTP). Heptadecane simulating the fragments of the polyethylene monomeric units was used as a second substance, B.

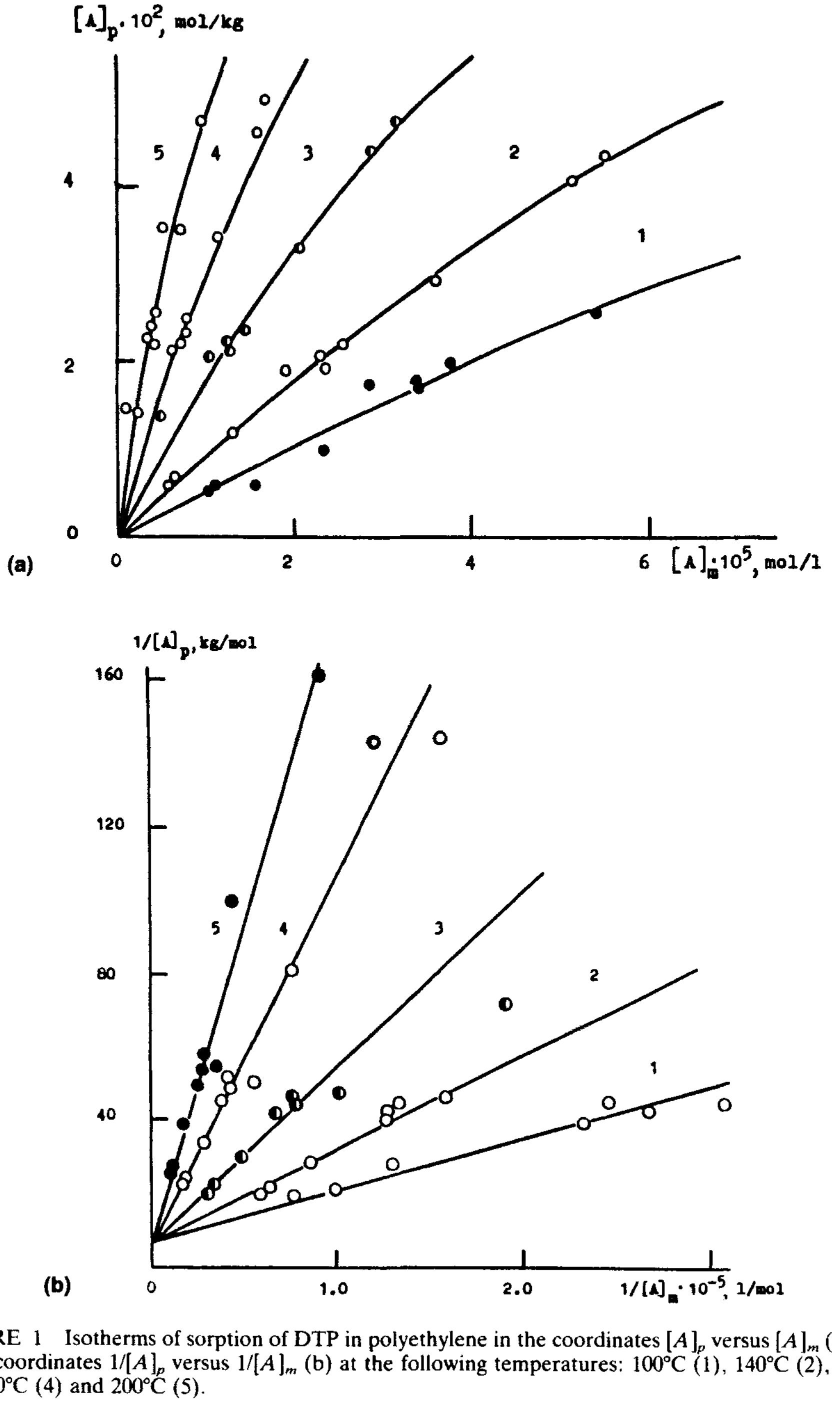

FIGURE 1 Isotherms of sorption of DTP in polyethylene in the coordinates $[A]_p$ versus $[A]_m$ (a) and in the coordinates $1/[A]_p$ versus $1/[A]_m$ (b) at the following temperatures: 100°C (1), 140°C (2), 160°C (3), 180°C (4) and 200°C (5).

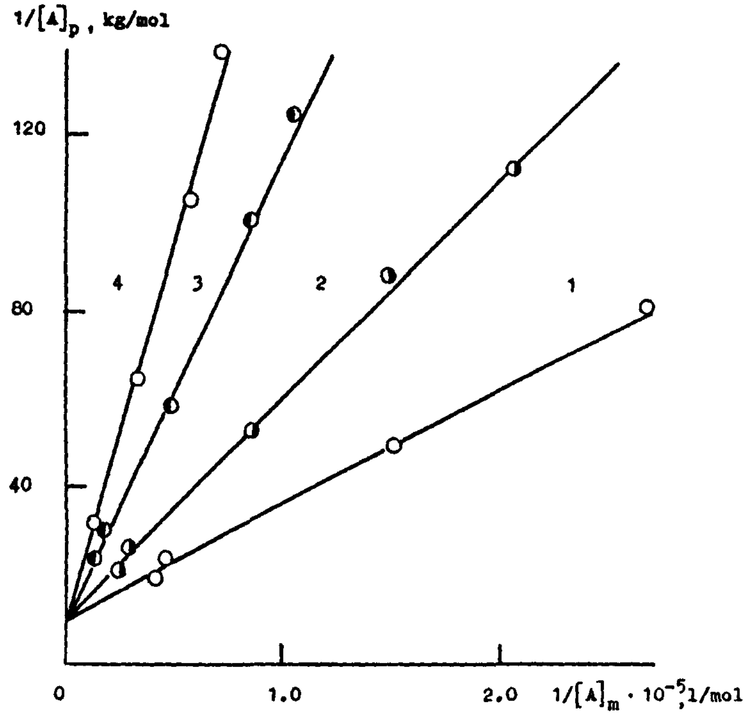

FIGURE 2 Isotherms of sorption of DTP in polyethylene in the presence of 1% of heptadecane in the coordinates $1/[A]_p$ versus $1/[A]_m$ at the following temperatures: 140°C (1), 160°C (2), 180°C (3) and 200°C (4).

EXPERIMENTAL

HDPE with molecular mass $\overline{M}_\omega = 2 \cdot 10^5$ in the form of powder has been used. The films with different content of heptadecane were prepared by pressing the powder in an inert medium at heating to 160°C. The film thickness was equal to 200 μm. The polymer films were saturated with the DTP vapors at a temperature of 90°C. To carry out sorption measurements, a glass tube provided with a quartz window was used, into which the polymer samples with a fixed concentration of the antioxidant was placed. Then the tube was vacuated and sealed. The tube was put into a thermostate at the temperature of testing and after 15–60 minutes the uv spectra were registered. The equilibrium concentration of the compound in the gas phase was then calculated. The concentration of the same additive in polymer was determined by the extraction with heptane and subsequent spectrophotometric analysis of DTP in the heptane solution.

RESULTS AND DISCUSSION

Figure 1 presents the isotherms of DTP sorption by polyethylene within a temperature range of 100–200°C in the $[A]_p$ versus $[A]_m$ coordinates. It can be seen

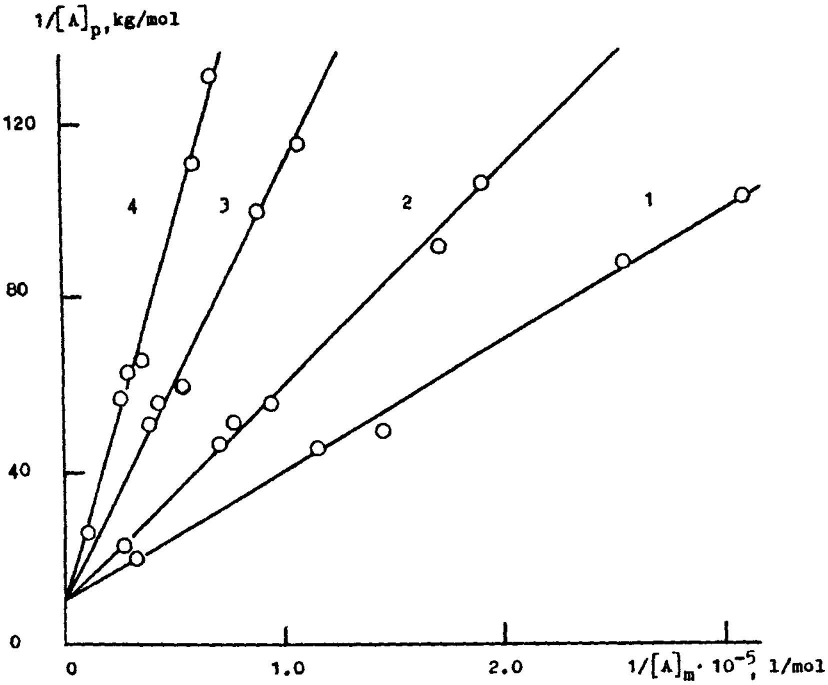

FIGURE 3 Isotherms of sorption of DTP in polyethylene in the presence of 1% of stearic acid in the coordinates $1/[A]_p$ versus $1/[A]_m$ at the following temperatures: 140°C (1), 160°C (2), 180°C (3) and 200°C (4).

from the figure, that the dependencies obtained are nonlinear, while those plotted in the $1/[A]_p$ versus $1/[A]_m$ coordinates give straight lines intercepting at the same point of the ordinate axis, differing from zero. In accordance with (4), the ordinate of this point is equal to $1/[Z]$. This means that the concentration of centers taking part in the sorption of DTP is equal to 0.15 mol/kg, and is independent of temperature. It does not change even at the polymer melting temperature.

A similar situation is observed when heptadecane or stearic acid are present in the polymer (Figures 2 and 3). It is of interest to note that the concentrations of the sorption centers in the polymer containing 1% ($4.2 \cdot 10^{-2}$ mol/kg) of heptadecane, or an equal amount of stearic acid, practically coincide and are equal to 0.1 mol/kg, i.e., they decrease significantly in the presence of the second substance in compliance with (7).

The value of the concentration of the centers participating in the sorption of DTP, $[Z]$, varies with the content of heptadecane in the polymer and passes over the minimum at heptadecane concentration of about 1%. The decrease of concentration of the sorption centers caused by heptadecane may be explained by the competition between heptadecane and DTP for the sorption centers Z. To this, in particular, testifies an approximate coincidence of the $[Z]$ decrease with the amount of heptadecane introduced into the polymer in the range of 0.5% (0.02 mol/kg) concentrations. The right section of a curve $[Z]$ versus the heptadecane concentration may be explained by the rearrangement of Z centers by heptadecane.

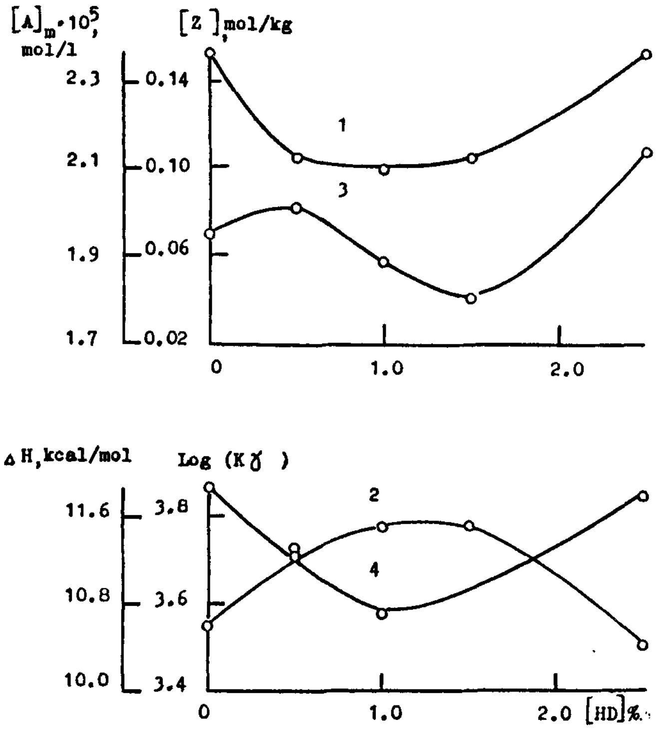

FIGURE 4 Dependence of $[Z]$ (1), $K\gamma$ (2), $[A]_m$ (3) and ΔH (4) on the content of heptadecane in polyethylene: the values $K\gamma$ and $[A]_m$ were obtained at 200°C.

In accordance with (4), the value $K_a\gamma = b$ characterizes the strength of bonding of an additive A with the sorption centers. As can be seen from Figure 4, with an increase of the heptadecane concentration in a polymer, the value $K_a\gamma$ changes antibately to $[Z]$, i.e., the low molecular weight hydrocarbon influences not only the concentration of the sorption centers, but also the properties of these centers. The opposite directions of the changes of $[Z]$ and $K\gamma$ result in a complex change of vapor pressure of DTP over the polymer on heptadecane concentration. The vapor pressure, i.e., the concentration of A in the gas phase, first increases, then decreases, and at the heptadecane concentrations over 1.5% increases again.

The similar dependencies of $[A]_m$ on the concentration of additives affecting the structure of a polymer were observed earlier in the work.[8]

It should be noted that the sorption proceeding in accordance with (3) is an exothermic process, therefore, when the temperature increases, the concentration $[A]_m$ corresponding to the same concentration of the substance A in a polymer (see Figures 1 and 2) also increases. A similar conclusion results from the positive values of the enthalpy of dissolution of DTP in polyethylene, which can be calculated from the temperature dependence of $K_a\gamma$ (Figure 5).

Though the value $K_a\gamma$ changes markedly when passing through the melting temperature, the dissolution heat ($\lambda_s = -\Delta H_s$) changes slightly.

Within a temperature range of 140–200°C, the value ΔH_s changes symbatically $[Z]$ with an increase of heptadecane concentration in a polymer. We suppose that

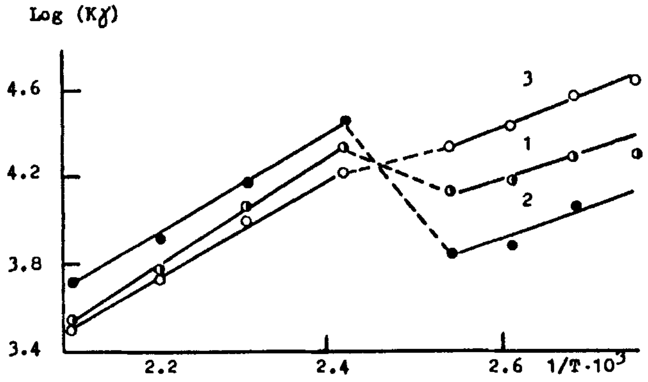

FIGURE 5 Temperature dependence of $K\gamma$ in the sorption of DTP in polyethylene in the absence of other additives (1) and in the presence of 1% of heptadecane (2) and 1% of stearic acid (3).

heptadecane taken in small concentrations (up to 1%) is sorbed with the centers accessible for DTP and the sorption of DTPh with such "occupied" centers demands additional energy required for expelling heptadecane from the sorption centers:

$$ZC_{17}H_{36} + DTP \rightleftharpoons ZDTP + C_{17}H_{36}.$$

Heptadecane being at high concentrations can rearrange the structure of a polymer in such a way that the sorption centers become more convenient for the DTP molecules:

$$Z + nC_{17}H_{36} \rightarrow Z^*(C_{17}H_{36})_n.$$

Thus the role of heptadecane dissolved in a polymer consists of the rearrangement of the polymer structure and of the change of the character of DTP distribution among the polymer elements.

References

1. D. R. Paul and W. J. Koros, *J. Polymer Sci., Polymer. Phys. Ed.*, **14**, 675 (1976).
2. Yu. A. Shlyapnikov, A. P. Mar'in, *Eur. Polym. J.*, **23**, 623 (1987).
3. R. M. Barrer, J. A. Barrie and J. Slater, *J. Polymer. Sci.*, **27**, 177 (1958).
4. W. R. Vieth, R. M. Tam and A. S. Michaels, *J. Coll. Interface Sci.*, **22**, 360 (1966).
5. R. J. Pace and A. Datyner, *J. Polymer Sci., Polymer Phys. Ed.*, **18**, No. 5, 1103–1124 (1980).
6. A. P. Mar'in and Yu. A. Shlyapnikov, *Vysokomol. Soedin.*, **29**, ser. A, No. 8, 1620 (1987).
7. I. A. Shlyapnikova, A. P. Mar'in, G. E. Zaikov and Yu. A. Shlyapnikov, *Vysokomol. Soedin.*, **27**, ser. A, No. 8, 1736 (1985).
8. E. A. Sviridova, A. P. Mar'in, S. G. Kiryushkin, M. S. Akutin and Yu. A. Shlyapnikov, *Vysokomol. Soedin.*, **30**, ser. A, No. 2, 419 (1988).