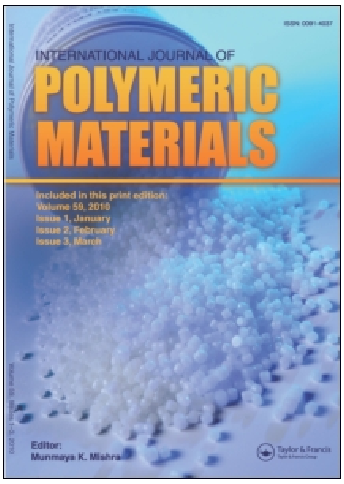

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Physical Chemistry of Topological Disorder: Complications at Additives Sorption by Polyethylene from Solutions

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Low-molecular compounds dissolved in polymers form complexes with sorption centers Z_i around various topological structures: knots and entanglements of the polymer chains. At simultaneous sorption of two or several compounds, A and B, the centers divide into three groups: the centers Z_a sorbing only A, Z_b sorbing only B, and centers Z_c which can sorb both A and B. Competition between compounds A and B for the centers of third type has been observed at sorption of several compounds by high-density polyethylene from hexane solutions.

At sorption by low-density polyethylene from isopropanol solutions the cases were observed where the introduction of the second additive increases the solubility of the first one in the polymer.

Keywords: Topological disorder; polyethylene; sorption; low-molecular compounds; sorption centers

Many polymeric materials contain low-molecular additives: plasticizers, dyes, stabilizers, etc. These additives when dissolved in a polymer are present there in either a true solution form or as immobile complexes with specific structures – the sorption centers Z_i [1, 2]. These centers exist both in "solid" polymer and in the polymer melt and their concentration is independent of temperature. This latter characteristic allows us to identify them as the elements of topological disorder; such as numerous knots and entanglements of the polymer chains [1–3].

Concentration of truly dissolved additive is usually negligible compared to that present in the centers, and we may assume that all additive dissolved in a polymer exists in it as complexes AZ_i, remembering in the same time that a certain, though very small concentration of mobile A molecules is necessary to explain its mobility. The concentration of mobile molecules in polymer $[A]$ is connected with the additive concentration in surrounding medium (solvent or vapors) $[A]_m$ by Henry law: $[A] = \gamma_a [A]_m$. Thus we can describe the process of additive sorption by one type of centers Z_i by equation

$$A + Z_i \overset{K_{ai}}{\rightleftharpoons} AZ_i \tag{1}$$

It follows from (1) that

$$[AZ_i] = \frac{K_{ai}[Z_i][A]}{1 + K_{ai}[A]} \tag{2}$$

or, if the polymer saturated from vapors or solution

$$[AZ_i] = \frac{K_{ai}\gamma_a[Z_i][A]_m}{1 + K_{ai}\gamma_a[A]_m} \tag{3}$$

If the set of centers Z_i exists in the polymer, this dependence will be described by the sum

$$[A]_p = \sum_i [AZ_i] = \sum_i \frac{K_{ai}\gamma_a[Z_i][A]_m}{1 + K_{ai}\gamma_a[A]_m} \tag{4}$$

According to the dependence (4), at low additive concentrations when $[A]_m \to 0$, $[A]_p = 0$, the initial slope is

$$\lim(d[A]_p/d[A]_m) = \gamma_a \sum K_{ai}[Z_i]. \tag{5}$$

and at high concentrations, i.e. if $[A]_m \to \infty$,

$$\lim([A]_p) = \sum [Z_i] = [Z]_a. \tag{6}$$

In most cases the expression (4) may be approximated by more simple one [1]

$$[A_p] = \frac{K_a \gamma_a [Z_a][A]_m}{1 + K_a \gamma_a [A]_m} \tag{7}$$

where K_a is the certain average meaning of equilibrium constants K_{ai} depending on the character of sorption centers distribution. According to (6), the meaning of $[Z_a]$ – the total concentration of centers capable of sorbing A – does not depend on this distribution.

Formula (7) may be transformed into the form more convenient for comparing with experiment:

$$\frac{1}{[A]_p} = \frac{1}{[Z_a]} + \frac{1}{K_{ai} \gamma_a [Z_a]} \times \frac{1}{[A]_m} \tag{8}$$

According to (8), the dependence of the additive concentration in polymer $[A]_p$ on its concentration in surrounding medium $[A]_m$ in the coordinates $1/[A]_p$ vs $1/[A]_m$ may be transformed into the straight line intersecting the ordinate axis in the point $y = 1/[Z_a]$ not coinciding with the coordinate origin.

The expression for sorption of any other compound B will be analogous to (7), but the set of centers Z_b will be different. In general case we may expect that the set of centers present in the polymer sample includes the centers capable of sorbing only A, those sorbing only B, and centers sorbing both A and B, and if we put the sample into solution containing both A and B the competition between these additives for these centers must result in decreasing concentration of one additive in the presence of another one. Denoting these latter centers Z_c, we may write

$$AZ_c + B \overset{K_c}{\rightleftharpoons} BZ_c + A \tag{9}$$

or, if each center Z_c can sorb several molecules of the same additive

$$A_n Z_c + mB \rightleftharpoons B_m Z_c + nA \tag{9a}$$

It follows from (9)–(9a) that the concentration of one additive (A) in the polymer will decrease with increasing concentration of another additive (B) in surrounding medium tending to a certain limit. Denoting the constants of equilibrium of sorption of additives A and B by the centers Z_c correspondingly K_{ca} and K_{cb}, we get the formula for dependence of concentration of A in centers Z_c $[A]_{cp}$ on $[A]_m$ and $[B]_m$

$$[A]_{cp} = \frac{K_{ac}\gamma_a[Z_c][A]_m}{1 + K_{ac}\gamma_a[A]_m + K_{bc}\gamma_b[B]_m} \tag{10}$$

This expression describes the variation of concentration of the additive A on concentrations of A and B in surrounding medium. Obviously the concentration of additive A in the centers Z_a remains independent of $[B]_m$.

In this work we studied the simultaneous sorption of two low-molecular compounds by high-density polyethylene from their solutions in hexane, which solvent may be considered as low-molecular model of the polymer, and in polar solvent iso-propanol.

EXPERIMENTAL

High-density polyethylene (HDPE), $M_\eta = 1.7 \times 10^5$, and low-density polyethylene (LDPE), $M_\eta = 6 \times 10^4$, were precipitated by methanol from toluene solution. The samples were films 0.010–0.011 cm thick prepared by pressing in the absence of oxygen with subsequent heating in vacuum (100 °C, 24 hours).

Low-molecular compounds were α-naphthol (I), and α-naphthylamine (II), purified by vacuum sublimation, phenylbenzoate (III), diphenylamine (IV), and diphenylmethane (V), purified by crystallization from alcohol. Concentrations of low-molecular compounds were analyzed by vacuum evaporation from samples with subsequent spectrophotometric analysis [4]. The additives were combined into pairs so that their spectral characteristics allowed us to simultaneously determine concentrations of both compounds. The solvents were n-hexane–low-molecular analog of polyethylene, and polar alcohol isopropanol.

The sorption of additives has been studied at 50 °C. As shown experimentally, it takes about 60 hours to reach the equilibrium additive concentration in the sample, but for greater reliability the time of samples saturation has been taken 120 hours.

RESULTS AND DISCUSSION

As shown in Figures 1–3, the sorption isotherms of all compounds studied (I–VI) by high-density polyethylene from hexane solutions plotted in the coordinates of expression (8) ($1/[A]_p$ vs $1/[A]_m$) are the straight lines in accordance with (8). The values of $[Z_a]$ for these

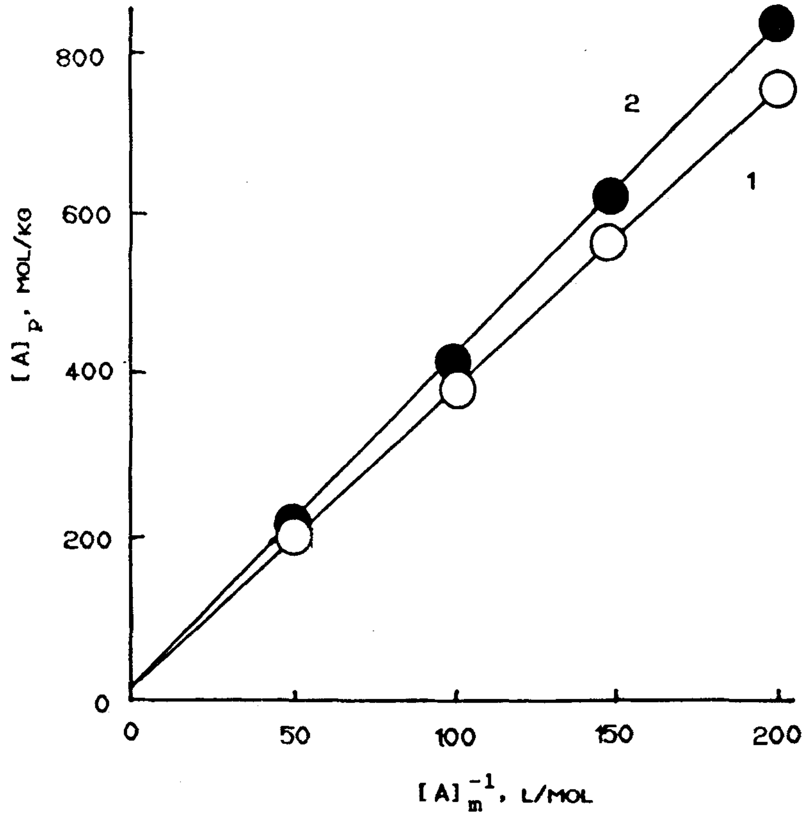

FIGURE 1 The sorption isotherms of α-naphthylamine (1) and α-naphthol (2) by high-density polyethylene from hexane solution in inverse coordinates $1/[A]_p$ vs $1/[A]_m$, temperature 50 °C.

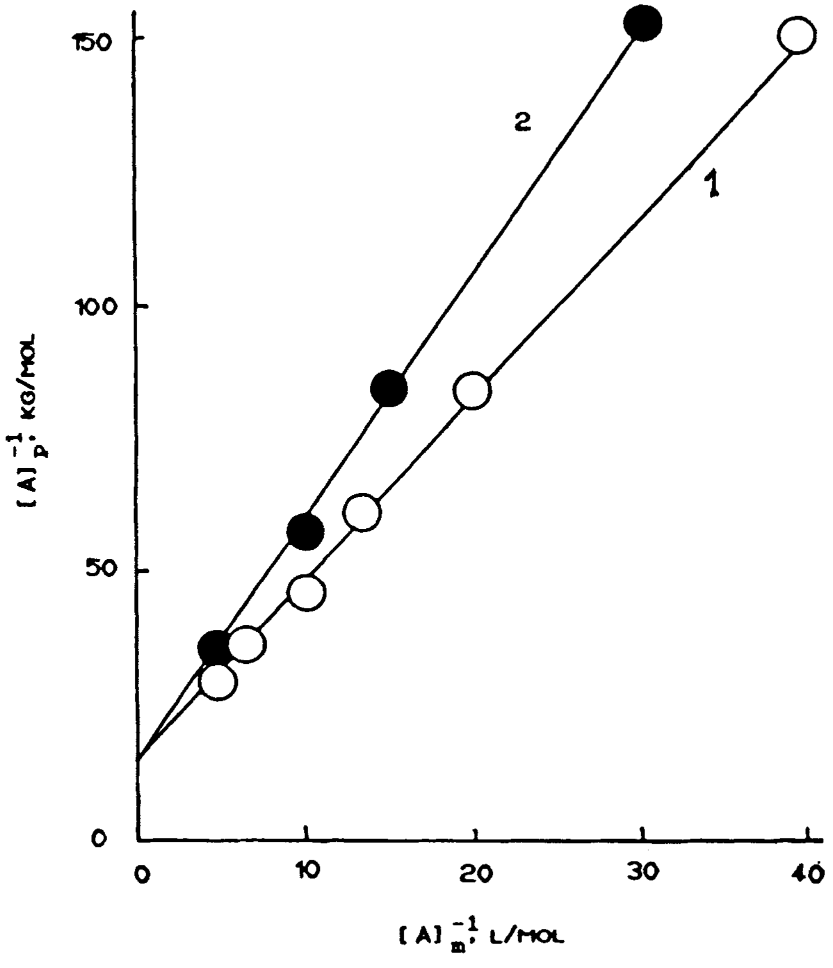

FIGURE 2 The sorption isotherms of phenylbenzoate *A* (1) and diphenylamine (2) by high-density polyethylene from hexane solution in coordinates $1/[A]_p$ vs $1/[A]_m$, 50 °C.

compounds are $[Z]_a = 0.10$ (I), 0.091 (II), 0.025 (III), 0.064 mol/kg (IV), 0.058 (V), and 0.083 (VI). The set of similar examples can be expanded. As shown in [5], these values depend on the nature of solvent playing the role of the second compound *B* in Eq. (9).

In subsequent experiments we immersed the samples of polyethylene into solutions containing the constant concentration of one additive (*A*), and variable–of another (*B*). As seen from Figures 3–6 the curves obtained divide into two groups: if the sorption proceeds from n-hexane that is in the presence of any second compound, the concentration of the first one (A) in the polymer decreases tending to a certain limit in accordance with Eq. (9). In the same time the concentration of the second compound (B) increases, though it remains smaller than in the absence of A.

Comparing the initial slopes of the curves $[A]_p$ vs $[B]_p$ in Figures 3–5 shows that the ratios $-\Delta[A]_p/\Delta[B]_p = n/m \gg 1$, i.e. the numbers of molecules of the first additive substituted by the second one is always much greater than 1. The simplest assumption is that some of the centers sorbing several molecules of one additive are very unstable and decompose first at penetration of one molecule of other additive (i.e. that $n \gg 1$; $m = 1$). On the other hand, we must take into account that the sorption of both additives proceeds from solvent which also can participate in the processes studied [5].

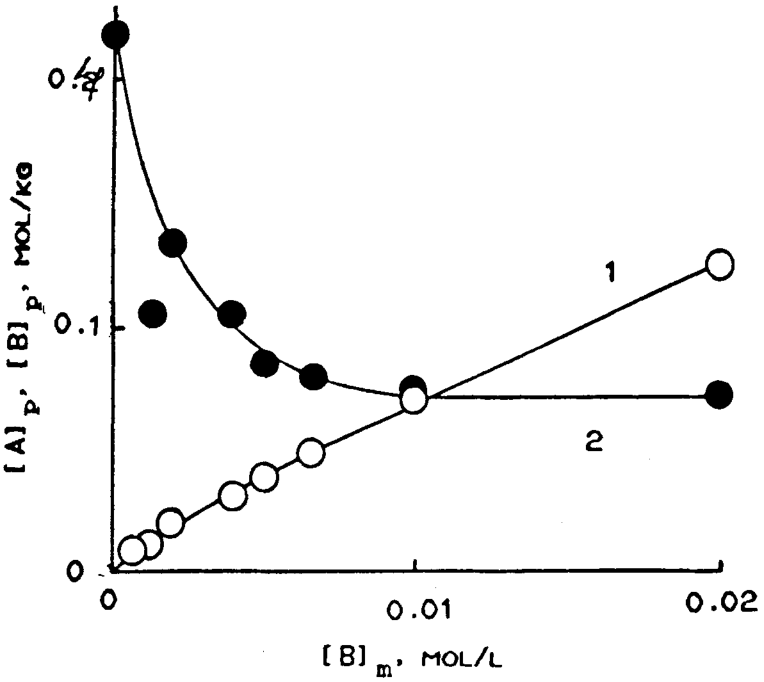

FIGURE 3 Equilibrium concentration of α-naphthylamine $[B]_p$ (1) and α-naphthol $[A]_p$ (2) in high-density polyethylene as functions of concentration of α-naphthylamine in hexane solution $[B]_m$ at $[A]_m = 0.02$ mol/l = const.

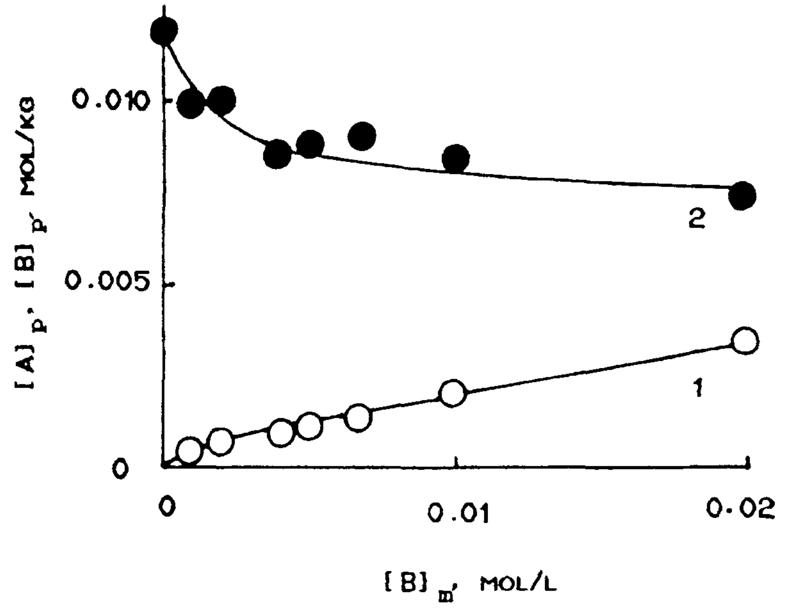

FIGURE 4 Equilibrium concentration of α-naphthol $[B]_p$ (1) and phenylbenzoate $[A]_p$ (2) in high-density polyethylene as functions of concentration of α-naphthylamine in hexane solution $[B]_m$ at $[A]_m = 0.05$ mol/l = const.

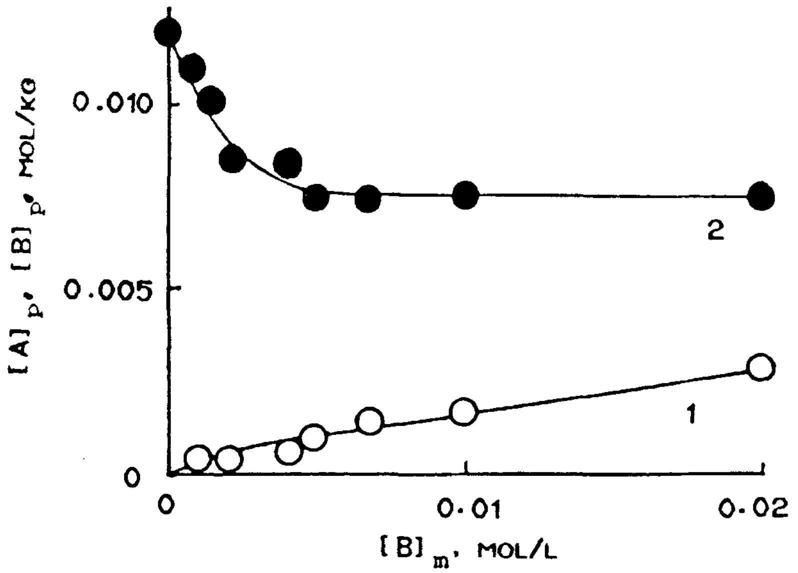

FIGURE 5 Equilibrium concentration of phenylbenzoate $[B]_p$ (1) and α-naphthylamine $[A]_p$ (2) in high-density polyethylene as functions of concentration of α-naphthylamine in haxane solution $[B]_m$ at $[A]_m = 0.05$ mol/l = const., 50 °C.

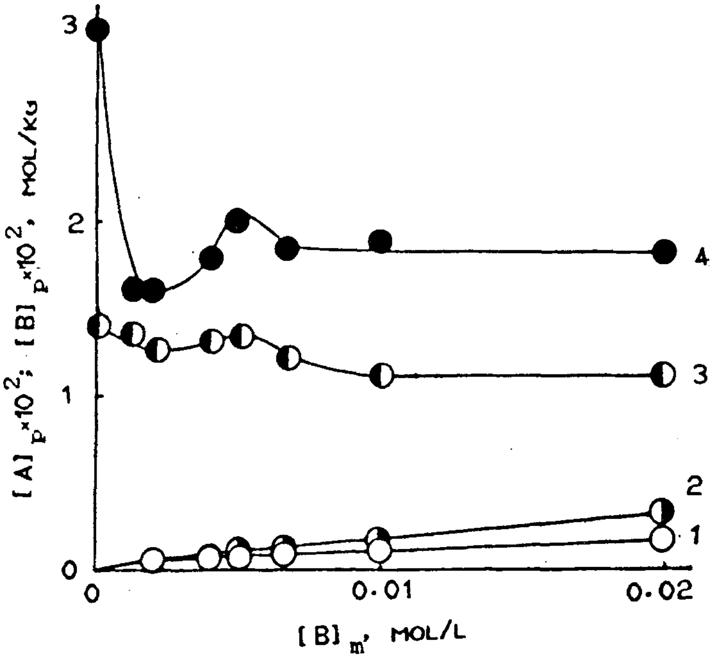

FIGURE 6 Equilibrium concentrations of α-naphthol $[B]_p$ (1, 2) and diphenylmethane $[A]_p$ (3, 4) in high-density polyethylene (1, 3) and low-density polyethylene (2, 4) as functions of the concentration of α-naphthol in its solution in isopropyl alcohol $[B]_m$ at $[A]_m = 0.20$ mol/l = const., 50 °C.

The analogies between curves in Figures 3, 4 and 5 show that the mutual substitution of different compounds in their solutions in polymers is a general phenomenon, though if additives are sorbed by relatively soft polyethylene and from low-molecular solvents its mechanism may be complicated and include not only mutual substitution of additives and solvent but also rearrangement of centers Z_i. It has been shown earlier [6] that the addition of the second additive – 'inert' compound – to the polymer containing low–molecular antioxidant increases the ratio of mobile (not bound with centers) antioxidant molecules in accordance with Eq. (9) or (9a) increasing thus the effectivity of the antioxidant.

On the other hand, at sorption from isopropanol solution concentration of the first additive $[A]_p$ at low $[B]_m$ decreases, but then, in the certain range of $[B]_p$ increases passing over maximum (Figs. 6 and 7). It may be seen that both equilibrium concentrations and maxima in

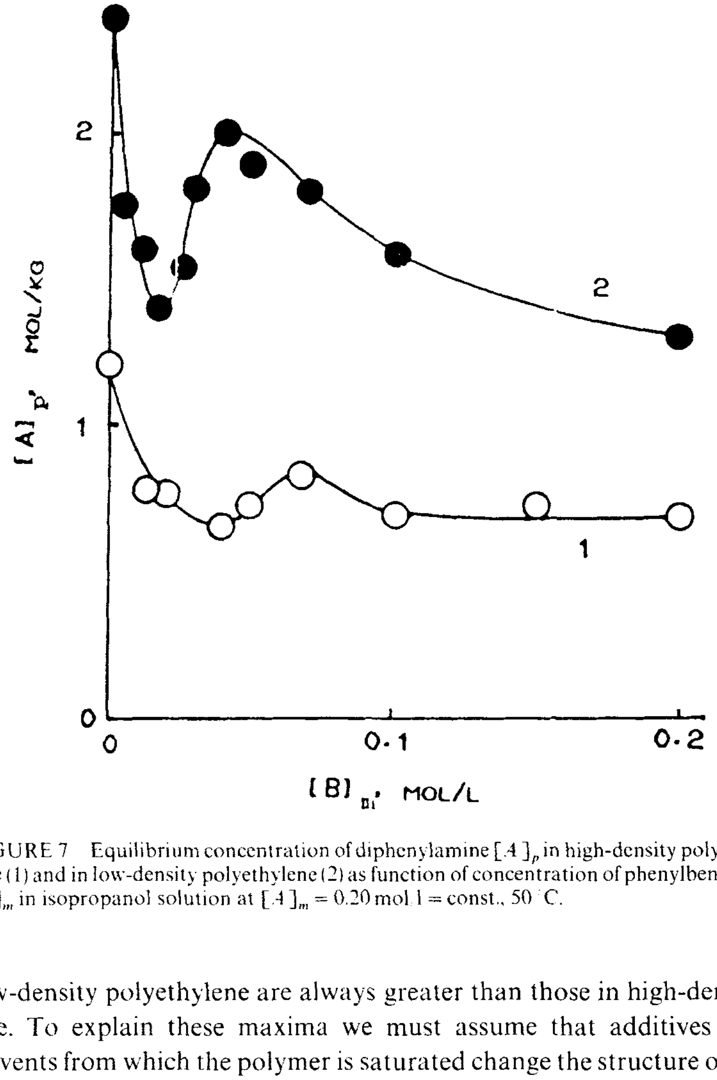

FIGURE 7 Equilibrium concentration of diphenylamine $[A]_p$ in high-density polyethylene (1) and in low-density polyethylene (2) as function of concentration of phenylbenzoate $[B]_m$ in isopropanol solution at $[A]_m = 0.20$ mol/l = const., 50°C.

low-density polyethylene are always greater than those in high-density one. To explain these maxima we must assume that additives and solvents from which the polymer is saturated change the structure of the sorption centers, more easily in low-density polyethylene where the polymer chains are more mobile. Otherwise it is not possible to explain by simple formation of complexes ABZ_{ab} the large absolute values of the ratio $\Delta[A]_p/\Delta[B]_p$ observed at simultaneous sorption of two additives.

As shown in [7, 8], the level of topological disorder, determining $[Z_a]$ values, varies at variation of conditions of polymer precipitation, otherwise the parameters of additive solubility depend on pre-history of the polymer sample. The condition of polymer precipitation must also affect other properties of the polymer.

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