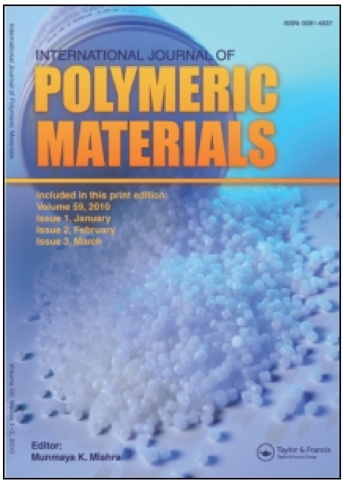

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Mikheev, Yu. A. , Guseva, L. N. and Zaikov, G. E.(1999) 'Sponge Effects at the Interaction of Polymers with Low-molecular Compounds', International Journal of Polymeric Materials, 43: 3, 169 — 193

To link to this Article: DOI: 10.1080/00914039908009684

URL: http://dx.doi.org/10.1080/00914039908009684

Intern. J. Polymeric Mater., 1999, Vol. 43, pp. 169–193
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Sponge Effects at the Interaction of Polymers with Low-molecular Compounds

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(Received 7 December 1997)

A competition among additives for a place in the polymer matrix under levelling effect of the blending enthalpy was found. The competition apparently contradicts the entropy nature of the mixtures exhibiting accelerated desorption of the added compound from films in a glassy- or jelly-like state. The effects considered cannot be treated by statistical of thermodynamics of solutions and the theory of "the chaos elements in the close order range". They are however, explainable by taking into account the specificity of the chain-sponge structure function. The processes of the equilibrium sorption of vaporized compounds by polymers are explained by the mechanism of structural entropic solvation and described by the equation of the micropore volume filling theory.

Keywords: Sorption; PMMA; cellulose triacetate; solubility; sponge polymer structure; low-molecular compounds

INTRODUCTION

It is common knowledge that some properties of highly elastic and melted polymers can be explained by statistical thermodynamics of flexible polymer chains [1]. Progress in this field leads to attempts of applying the liquid-phase concepts to glassy and gelled polymer systems. However, the structural model visualizing a polymer as a high-molecular liquid is inadequate for polymer objects displaying the supermolecular organization such as the spongy carcass consisting of

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aggregated chains. Existence of supermolecular carcass is responsible for the failure of homogeneous statistics to explain, for example, the features of cold flow, memory effects and non-Newton flow of melts [2], plasticization anomalies, anti-plasticization and properties of polymer gels [3, 4], sorption [5], and the phenomenon of thermodynamic affinity splitting in the single "polymer-nonsolvent liquid" pair [6].

For some time, the deduced energetic effect of polymer chain compression at dissolution was considered as the achievement of the modernized Flory theory. It seemed that this would solve the problem of exothermic characteristics of polymer mixing with its hydrated monomer. In the theory of low-molecular liquid mixing the equal parameters of solubility must provide its athermal characteristics, and the different ones–endothermic characteristics. However, as it was shown experimentally in [7], the thermodynamic interconnection (acceptable for liquids), between the heat evolution and bulk contraction of the solution is not applicable for polymer dissolution. The real exothermic effect for polystyrene in its hydrated monomers displayed a specific dependence on dissolution temperature, but it did not depend on the compression of the samples by external forces. It is explained in [8] by the transformation of a chain-sponge domains carcass into a colloid dispersion of intracarcass liquid drops disappearing during dissolution.

Recently a series of works appeared, in which an attempt to avoid the liquid phase approaches was made. A great attention in them is paid to "the elements of the damage in the zones with close order" [9, 10]. The authors of [9, 10] studied sorption of aromatic compound vapors by films and melts of PE (polyethylene) and PP (polypropylene). They observed parts of Langmuir-like isotherms with their specific exothermic characteristics. On the contrary, different endothermic characteristics was observed at similar parts of curves of the equilibrium sorption from alcoholic solutions of the same compounds [11, 12]. The results were explained by adsorption of aromatic compounds to a limited number of rigid centers–the points of the regularity damage in the structures with the crystal-like packing of chain segments. The suggested supposition is probable because crystallite elements are rather stable and are preserved in the melts of polyolefins in a wide temperature range [13].

Elaborating one of the variants of colloid-chemical modeling of the non-crystalline polymer phase, the authors of [9–12] have limited their considerations to a narrow range of easily crystallizing objects and did not take into account the role of chain-sponge structures [6, 8, 14]. The present review presents the data on the chain sponge responsibility for the processes of interaction with low-molecular compounds which are anomalous from the point of view of the liquid-phase thermodynamics and the theory of rigid sorption centers.

EXPERIMENTAL TECHNIQUE

Optically transparent non-crystalline films of polymethylmethacrylate (PMMA) with $M_n = 140000$ and cellulose triacetate (CTA) with $M_v = 330000$ were used. They contained different amount of spectrally pure additives of aromatic compounds: liquid plasticizer of dibutylphthalate (DBP, $T_{\text{boil}} = 340°\text{C}$) and naphthalene ($T_{\text{boil}} = 80.2°\text{C}$). Films of blend 10–50 µm thick were prepared from the components dissolved in methylenechloride (MC) and chloroform by vaporizing solvents in Petri dishes. All the compounds used are characterized in literature by close solubility $\delta(J/\text{cm}^3)^{0.5}$: both polymers give 19.0; methylenechloride – 19.86 chloroform – 19.0; DBP – 19.8; naphthalene – 20.4 (in accordance with [15] is accepted as the same of nitrobenzene). Spectrally pure heptane ($\delta = 15.3$) and distilled water ($\delta = 46.4$) were also used [16]. Spontaneous and stimulated desorption of additives were studied *via* the change of their UV-absorption by "Specord UV-Vis" device. Diffusion coefficients D_d were calculated from the linear plots of the admixture optical density change, D, during desorption

$$\left(1 - \frac{D}{D_0}\right) = \left(\frac{4}{L} \cdot \frac{D_d t}{\pi}\right)^{0.5} \quad \text{at} \quad \frac{D}{D_0} < 0.5.$$

Here D_0 is the initial value of D. Values of D were corresponded to the maxima of absorption bands: 34400 or 32200 cm^{-1} for naphthalene and 36600 cm^{-1} for DBP. DBP release from the films with its high concentration was calculated by the equation:

$$\frac{D}{D_0} = \left(\frac{8}{\pi^2}\right) \exp\left(\frac{D_d \pi^2 t}{L^2}\right),$$

which is valid at $(D/D_0) > 0.4$. For both equations L is the thickness of the film; π is 3.1416; t is the current time.

Desorption of naphthalene possess an initial period, during which the process rate is extremely low. At heating in air of CTA films with 1% naphthalene this period may reach 100 min, but it decreases as the concentration increases and also in the presence of DBP and film heated in water. The reason for process instability in the initial stage originates in the fact that during the film formation by solvent evaporation the additives migrate from surface layers, from the side of air and silicate glass into the film depth. This phenomenon causes the formation of a relatively rigid crust with decreased entropy of a polymer-chain sponge. This also implies a decrease of the admixture solubility. The resulting inhomogeneity is fixed as a result of drying and vitrification of the samples. In this case, the transition of the desorption into the stationary diffusion stage requires a definite time.

RESULTS AND DISCUSSION

According to statistical thermodynamics, equality of solubility indexes excludes the role of the enthalpic factor at mixing of liquids, and the spontaneous mixing is bound to an increase of the solution entropy. A mixture formed from a pair of such components does not decrease the affinity of components under the effect of the third component possessing the same solubility. Possessing no preferable interaction with one or another component, the third one cannot decrease their affinity while increasing the total entropy of the mixture. What concerns the water effect on the binary mixture of hydrophobic oleophils, there are also no reasons selective exudation of one of them, because water molecules are actively exuded from the hydrophobic mixture. At the same time, experiments prove the antagonism of different oleophils and the existence of hydrostimulated desorption from hydrophobic polymers.

INTRASTRUCTURAL EXUDATION

Interesting processes may be observed already at the preparation of films with DBP and naphthalene. Equilibrium sorption of these compounds by CTA and PMMA films reaches only several percents, but up to 30% of naphthalene and 90% of DBP are introduced into them from solutions in MC or chloroform. It is characteristic that CTA gels with 90% of DBP are insoluble in the excess of liquid DBP even at $T = 100°C$ [6]. Dependency of the result of mixing on its way of performance does not respond to the statistic thermodynamics and is neglected in determination of the polymer solubility index. For this index the parameter of the liquid is accepted, which provides the maximum mixing degree independently on the solvent or applied thermomechanical treatment.

Glassy CTA and PMMA films which contain one of the above mentioned compounds release an additive extremely slow by preserving its initial amount during many weeks and months. Taking into account the absence of energetic reasons for a competition between those additives for the links of macromolecules or sorption rigid centers one should also expect enough stability of the films, which contain both compounds. However one may succeed in introducing 5% of naphthalene into CTA films only if the concentration of simultaneously introduced DBP does not exceed 15%. If DBP concentration is 20%, most of naphthalene escapes during the film formation.

The process of naphthalene exudation from CTA and PMMA films formed with 30% of DBP was studied in more detail. Solutions were prepared taking 5.5% of naphthalene per dry residue. In this case the solvent was evaporated in open Petri cups from 0.8 mm thick layer of the solution. Glassy films 45 μm thick were obtained after 1 or 2 hours, and a day after naphthalene concentration in them was found 2% of the initial amount only. At the same time, naphthalene residue at free naphthalene evaporation from stationary liquid layer of DBP yielded 3% of its initial amount for the same period of time. So the rate of naphthalene exusion from glassy films with DBP was not lower than from that of liquid DBP, whereas in the absence of DBP the loss was not observed during MC evaporation and during long-term storage of the films with naphthalene concentration up to 20%.

Exusive activity of DBP is also observed at its concentration below 15%. This is confirmed by the data shown in Figure 1. Curve 1 on Figure 1 represents the dependency of naphthalene diffusion coefficient (D_n, cm^2/s) on its concentration (C_n, %):

$$D_n = 1.3 \cdot 10^{12} C_n,$$

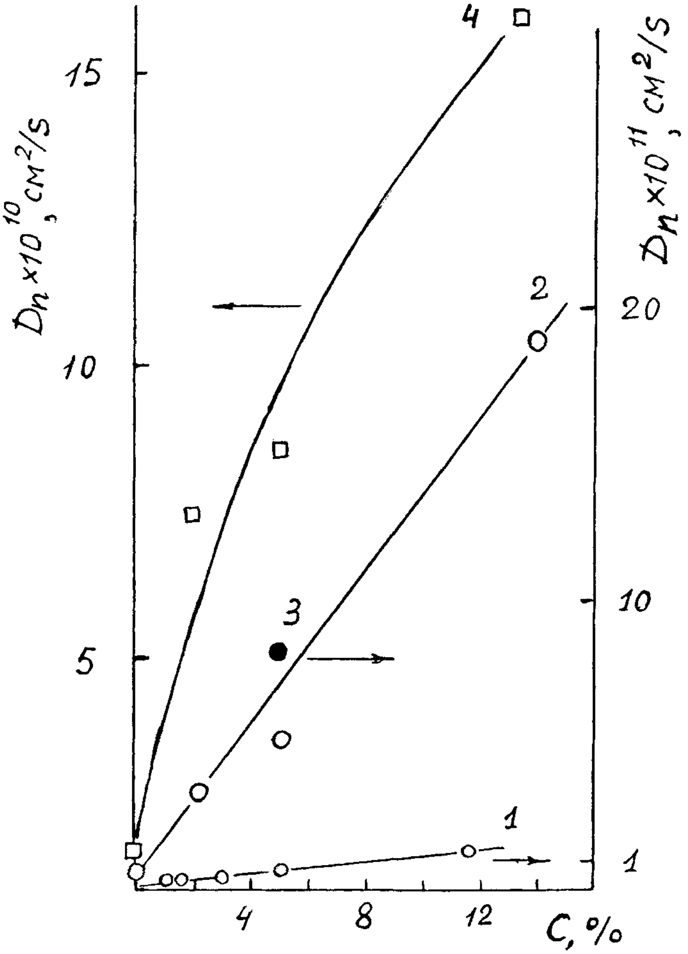

FIGURE 1 Dependency of naphthalene diffusion coefficient from CTA films with naphthalene (1) and CTA films with DBP and 5% of naphthalene (2–4) on the concentration of naphthalene (1) and DBP (2–4) at desorption in air (1, 2), liquid DBP (3) and water (4) at temperature of 99°C (1–3) and 80°C (4).

and straight line 2 – on DBP concentration (C_D, %) for $C_n = 5\%$:

$$D_n = 0.6 \cdot 10^{-11} C_n + 1.3 \cdot 10^{-11} C_D.$$

Thus, DBP added to the CTA films caused an order higher effect on desorption than naphthalene itself.

The effect observed may be formally related to the plasticization effect. However, it is characterized by the process proceeding in glassy films. Moreover, D_n constants of desorption in air and in liquid DBP heated up to 99°C (Fig. 1, point 3) are practically equal. Consequently, in this case we may consider the structural-heterogeneous plasticization of the type reported in [17], according to an increase of the isomerization rate of benzospyranic dyes on glassy PMMA. Despite the intrinsic rigidity of the glassy samples, the isomerization rate increased up to its liquid-phase values in the presence of a small amount of plasticizers.

Physical sense of such "intrastructural" plasticization may be bound to the autonomous activation of dynamics of the chain-sponge domain enclosed in the cells of rigid paracrystalline carcass which is insoluble in DBP even at 99°C.

EXTERNAL EXUDATION OF OLEOPHILS

In the above described experiments with the solution of four components, the solvent (MC or chloroform) evaporated first, then naphthalene, and DBP evaporated at the lowest rate. At the same time, DBP may is also easily removable from films by exchange technique, for example, by liquid heptane. The latter is not the solvent for CTA and PMMA and is sorbed by pure CTA films in amounts not exceeding 1 mol/kg concentration, but when removing DBP it is combined with the polymer in significantly higher amounts.

The experiments have shown that the coefficient of DBP diffusion (D_D) from CTA films into heptane at 95°C increases with the DBP concentration: $2.0 \cdot 10^{-12}$, $8.0 \cdot 10^{-11}$ and $1.0 \cdot 10^{-9}$ cm^2/s for C_D = 1.4, 14.0 and 55.0%, respectively. Desorption from the films with 19% of DBP in air gives low $D_D = 7.0 \cdot 10^{-13}$ cm^2/s. It is practically unobservable at 1.4% during 50 hours, but in heptane the plasticizer exudation from the films with $C_D > 50\%$ is completed in 1.5 hours.

In the latter case the films retain the initial thickness and volume. This demonstrates another way for blending the admixture with the polymer, whose spongy system is kept swollen by the heptane osmotic pressure. The amount of the latter reaching 6 mol/kg significantly exceeds the equilibrium sorption by the pure polymer.

The experiment with heptane proves the formation of a microporous adsorbent structure in polymeric chain-sponge domains. It is incorporated more or less rigidly by domains of the paracrystalline carcass, composed during solvent evaporation, and responds to current conditions of the carcass. The latter may significantly affect the final balance between spongy domains and those of the paracrystalline carcass, which is expressed, for example, in the values of the above mentioned coefficient D_D. At the same time, sufficient carcass rigidity is the factor that causes preservation of microporosity of the heptane-stabilized samples at DBP exudation even after its evaporation.

It should be mentioned that some facts connected to the chain-sponge structure are known for a long time. For example, Figure 2 shows the data from the work [18] on the effect of additive fillers on the equilibrium sorption of benzophenon (vapors, 30°C) by glassy polycarbonate (PC) films. One may observe that oligomeric oxypropyleneglycole (Fig. 2, Curve 1) and PC analog (Fig. 2 Curve 2) decrease the sorption. At the same time, stylbene–the aromatic compound similar in its molecular structure, significantly increases sorption, but is simultaneously completely removed from the films [18]. Thus, participating in the formation of sponge micropores on the stage of supermolecular carcass self-mounting stylbene causes a sorption increase for similar sized benzophenone molecules by indirectly providing places in the sponge, as it is the case of DBP substitution by heptane in CTA films.

In this case, the results of the work [19] should be mentioned, in which the indirect ways of polyvinylchloride combination with alcohols-precipitants are described. Great amounts of methanol, ethanol, *n*-propanol, isopropanol, butanol, isobutanol, and 2-ethylhexanol accumulate into the polymer matrix during exudation of DBP or dioctylphthalate, preliminary introduced into the polymer.

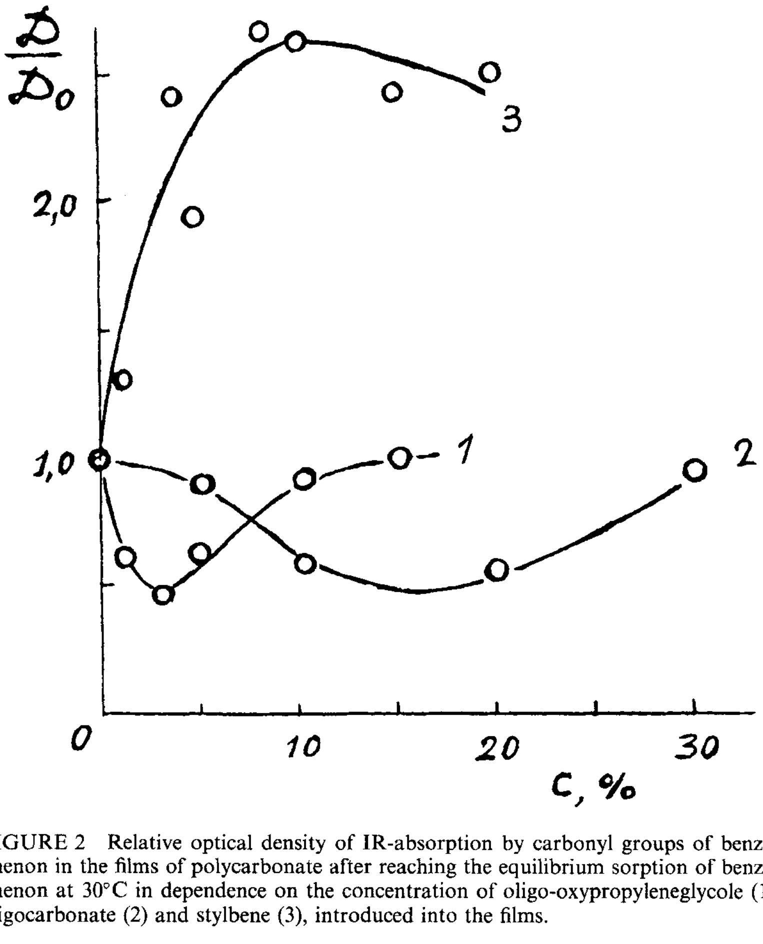

FIGURE 2 Relative optical density of IR-absorption by carbonyl groups of benzophenon in the films of polycarbonate after reaching the equilibrium sorption of benzophenon at 30°C in dependence on the concentration of oligo-oxypropyleneglycole (1), oligocarbonate (2) and stylbene (3), introduced into the films.

The structural similarity of plasticized and glassy polymers with additives to microporous sorbents was obtained by the NMR technique [20] and ESR [21]. Moreover, the important role of the microporous structure formed in the polymer during formation using various solvents was shown by mechanical tension tests of the films of CTA, PMMA and other polymers [22, 23]. However, the conclusion about the role of the chain-sponge carcass-micellar structure and its functions was not formulated. At the present time properties of the molecular sponge are rather clear. That allowed to disclose the physical sense of a list of non-understandable structural-physical [6, 8, 24] and chemico-physical effects [14, 24].

EXUDATION EFFECT OF WATER

Equilibrium sorption of water by pure CTA and PMMA films reaches 11% and 2.3%, respectively, at $P/P_s = 1$, but decreases in the presence of a large amount of DBP. Taking into account that DBP and naphthalene are highly hydrophobic compounds as liquid analogs of CTA and PMMA, no water effect on the structure and composition of two-or-three-component mixtures of oleophils with no stimulation of the selective exudation of one of them is anticipated on the basis of the liquid-phase thermodynamics. At the same time, water removes DBP from both glassy and gel films of both polymers. Exuded plasticizer covers the film surface by extremely small drops increasing the optical density by means of light losses through reflection and refraction. Those drops were removed using filtering paper during the experiment.

At 95°C water is able to remove DBP completely from both glassy and gelled films. The process in gels is accompanied by a significant decrease of the thickness (and bulk) of the samples (by a factor of two–three). Therefore, at the end of the process polymer chains in the sample are packed as in usual glassy films. In this case, the apparent coefficients of DBP diffusion calculated for the initial film thickness do not depend on the plasticizer concentration, and give $(2 \pm 1) \cdot 10^{-11}$ cm^2/s at $C_d = 1.4$; 19; 43; 65; 86%. Thus in accordance with the diffusion constants, the efficiency of external exudation inverted: at $C_d = 1.4\%$, water is more active than heptane, and at 14% and higher, heptane becomes more active than water.

The difference between water and heptane is not reflected only in values of D_d coefficients, but also in mechanical work of the material deformation and thickening of polymer chain packing. The osmotic pressure of heptane preserves the microporosity, preset by a plasticizer, and provides only the fluctuational action of stimulated DBP exudation, whereas osmotic pressure of water also provides an endothermic process of isothermal matrix compression. But both these situations are, by their physical sense, outside the domain of the statistical thermodynamics and the concept of the competition for structurally stationary sorption centers. In reality the oleophil, heptane, preserves the microporous sponge formed on that stage of the carcass mounting, and oleophobic water eliminates microporosity, set by the plasticizer, simultaneously with DBP removal.

Water also accelerates naphthalene desorption. At 99°C it affects CTA films with 1% of naphthalene stronger than heptane, which is confirmed by D_n coefficients: $1 \cdot 10^{-12}$ in air, $3 \cdot 10^{-10}$ in water, and $1 \cdot 10^{-11}\,\mathrm{cm}^2/\mathrm{s}$ in heptane. At the concentration of 11.4% desorption in air gives the diffusion coefficient of $1.6 \cdot 10^{-11}\,\mathrm{cm}^2/\mathrm{s}$ in air and $1.5 \cdot 10^{-9}\,\mathrm{cm}^2/\mathrm{s}$ in water.

An increase of hydrophobicity of CTA films with 5% of naphthalene *via* introduction of 5% DBP significantly increases water influence. This is shown in Figure 1, Curve 4 for hydrostimulated process at 80°C. It is seen that Curve 4 lies above the straight line 2, which represents desorption from the same films in air and in liquid DBP, but at 99°C. The strong effect of hydrostimulation observed (by hundreds and thousands of times stronger) cannot be explained from the point of view of homogeneous oleophil solution, because wettability of fatty surfaces by water is extremely low and becomes lower with temperature.

According to the homogeneous-statistic definition, the role of the enthalpic factor is excluded in the mixtures of used oleophils, but it is very important for their interaction with water, because very high δ-value of water leads to a significant endothermic characteristics of its mixing with fats. Neither the homogeneous solution theory, nor the theory of stationary centers of "irregularity in stable regularity zones" (*i.e.*, in colloid structures with fatty surfaces) is able to explain the reasons of stimulated exudation of any oleophil by water. These theories postulates that this phenomenon is connected with the decrease of mixture entropy in the absence of absolutely necessary decrease of the free energy (the Gibbs potential). The necessary decrease would be provided at the expense of the correspondent exothermic characteristics, which are impossible in the present case.

The picture described may be connected with the effect of a sponge, which is pressed out by osmotic pressure of water. The primary polymer-chain sponge contains an oleophil, whose molecules are weakly linked to the surrounding segments. Quasi-equilibrium state of additive molecules in the sponge is maintained through the osmotic equilibrium with vapors of the additive above the film, and also by means of structural reorganization of sponge chains under pressure of additive molecules. The reorganization is determined by the possibilities of conformational changes of sponge chains, which provide a definite increase of the entropy. Possessing such properties, the sponge is somewhat indifferent to chemical composition of captured molecules. Thus, the action of water is promoted by high activity of its vapors above the films and by respectively higher osmotic pressure comparing with the additive oleophils.

Relative indifference of the sponge to the chemical nature of captured additives is also shown by hydrostimulated desorption of hydrophilic compounds. For example, exudation of hydrogen peroxide activated by water from the samples of PMMA, swollen in it was observed in the work [26]. Hydrogen peroxide possesses the solubility index of $45.2(\mathrm{J/cm^3})^{0.5}$, which is practically equal to that of water, and mixes with water at any ratio. According to the data from the work [26], spontaneous desorption of water and hydrogen peroxide from PMMA films in air possesses diffusion coefficients of $3 \cdot 10^{-8}$ and $9 \cdot 10^{-8}\,\mathrm{cm^2/min}$, respectively. Hydrogen peroxide plasticizes the polymer, that is why it possesses higher diffusion coefficient, but much higher coefficient was found for the peroxide desorption from films, placed into water- and $3.5 \cdot 10^{-4}\,\mathrm{cm^2/min}$.

EFFECTS WITH PARTICIPATION OF POLYOLEFINS

The important role of stable centers of localized adsorption for the films and melts of polyolefins is noted in the works [9–12]. Such centers are known to adsorb additives due to enthalpic component of the Gibbs potential, *i.e.*, the "center-additive" bond energy capable of overwhelming the decrease of the entropic component bound to the additive molecule transition from liquid into solid state [27, 28].

In this connection the results of the works [11, 12] are of interest. These works reported a change of the heat effect sign of the aromatic substance sorption by polypropylene when the process is changed from vapors of these substances to alcoholic solutions. Endothermic characteristics of the stabilizer, phenyl-beta-naphthylamine (PNA), sorption from alcohol was found 18 kcal/mol. To change the physical structure, different amounts of the same stabilizer were introduced into the polymer melt. Afterwards the films were pressed and after their cooling the additive was extracted by alcohol in the Soxhlett device until complete purification. The films prepared in this manner displayed a characteristic change in sorption isotherms (shown in Fig. 3). But the endothermic characteristics of the process were kept constant giving the value of $\Delta H = +15\,\text{kcal/mol}$.

Though the endothermic characteristics are unfavorable for sorption, the process with alcohol is spontaneous. Moreover, the sorption increases after the polymer treatment (Fig. 3), indicating the structural memory effect.

As it is known, the driving force of the spontaneous process is a decrease of the Gibbs potential of the system $\Delta G = \Delta H - T\Delta S$. The sorption from solutions evidences $\Delta H > 0$ [11, 12]. At the same time the change of entropy is negative ($\Delta S < 0$) because the additive molecules have to lose the freedom of spatial motion on linking to rigid centers. This combination is accompanied by the increase of Gibbs potential that excludes the sorption.

The sorption from alcoholic solutions reflects the action of the mechanism, which provides an entropy increase with the correspondent ratios: $\Delta G < 0$, $\Delta H < T\Delta S$, caused by the polymer-chain sponge capability for the transformation into the state with higher number of chain conformations.

The accounting of this "reorganization" also allows us to explain the memory effect, the consequences of which are shown in Figure 3. The curves in Figure 3 show a significant increase of PNA sorption as a result of PNA treatment of PP melt, and they run together into one straight line passing the coordinate center. This line is the border of the set of curves which become straight as the structural memory effect increases under the amount of the stabilizer introduced into the melt.

According to the theory of sorption rigid centers [9, 12], the curve set in Figure 3 must not have a general tangent, but must diverge from the center of coordinates. In addition, a curve with higher limit must differ by proportionally higher slope of the tangent to the initial point. This is confirmed by the theoretical equation of the equilibrium sorption:

$$[A]_n = \frac{a[A]_c}{(1 + b[A]_c)}, \qquad (1)$$

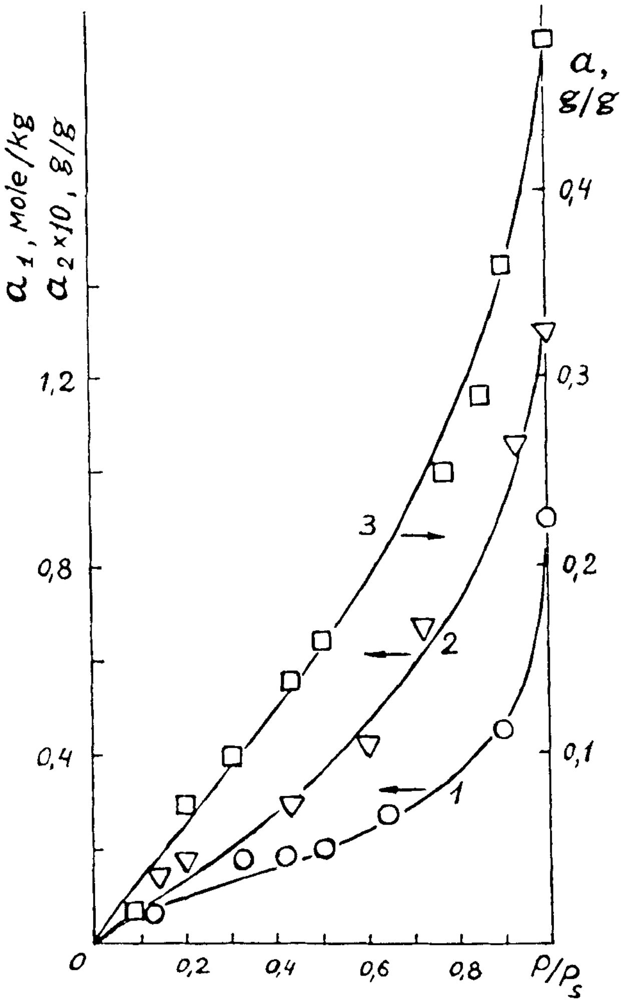

FIGURE 3 Dependency of $[A]_n$ on $[A]_c$ at the concentration A in the initial polymer melt of 0 (1), 0.22 (2), 0.34 (3), 0.44 (4), and 0.80 mol/kg (5) at 60°C.

which at low value $(b[A]_c) \to 0$ transforms into the straight line equation

$$[A]_n = a[A]_c = \gamma K_a[Z][A]_c,$$

where $[A]_n$ and $[A]_c$ are concentrations of the stabilizer in polymer and solution, respectively; $a = \gamma K_a [Z]$; $b = \gamma K_a$; γ is the Henry coefficient; K_a is the equilibrium constant of the reversible reaction between the additives and sorption centers. $[Z]$ is the sorption center concentration.

It follows from that theoretical expression that slope of the line, the tangent to the initial isotherm point, must increase in proportion to $[Z]$.

The independence of the slope of linear parts of the curves in Figure 3 on the limit sorption, as well as the spontaneous type of the process with endothermic characteristics, disproves the considered theory and turns us to the polymer-chain sponge concept.

In the new approach it should be taken into account that freezing of the PP melt with stabilizer makes additives to associate and form a colloid dispersion. A thin disperse phase is known to be different from that of large particles due to higher vapor pressure: the lower is the curvature radius r of the particle surface, the higher is the equilibrium vapor pressure above it [27]:

$$\ln\left(\frac{P_g}{P}\right) = \frac{2\sigma V_m}{RTr}.$$

Here P and P_g are vapor pressures above plain and curved surfaces, respectively; σ is the surface tension; V_m is the molar volume of the additive.

The increased vapor pressure P_g is compensated by negative pressure of sponge chains, which encapsulate the dispersion particles. In the equilibrium it strives to the minimum, making the particles to coagulate with a decrease of total interface.

Prints–cavities of the particles yielded from the melt remain in the PP matrix after their extraction by alcohol. The surface of these particle seem to persist in the prints the formation of future sorption centers. One may assume that the number of future centers is proportional to the surface square of the particles of the extracted colloid dispersion and that their amount increases with lowering of the equilibrium pressure P_g:

$$[Z] = a\left(\frac{P}{P_g}\right) = a\exp\left(-\frac{2\sigma V_m}{RTr}\right). \tag{2}$$

Here a is the coefficient of proportion.

Polymer cavities are filled with alcohol and additives during stabilizer sorption from the alcoholic solution, the additive adsorbing on the curved interface. Stabilizer molecules form flakes with negative curvature covering the interface of the cavities filled with the solution. That is the reason why their solubility in alcohol decreases if compared with the plain surface [27]:

$$\ln\frac{C_g}{C} = -\left(\frac{2\sigma_c V_m}{RTr}\right).$$

Here C_g and C are equilibrium concentrations of stabilizer in alcoholic solution above curved and plain surfaces, respectively; σ_c is the interphase tension.

The situation described may be combined with the equations from the theory [9, 12]. The equilibrium constant K_a of the reversible binding of centers Z to additive molecules $A + Z \rightleftharpoons AZ$ is opposite by its sense to the constant K_p of the dissolution equilibrium:

$$K_p = \frac{C_g}{C} = \frac{1}{K_a},$$

that leads to

$$K_a = \frac{C}{C_g} = \exp\left(\frac{2\sigma_c V_m}{RTr}\right).$$

Substituting expression for K_a and $[Z]$ Eq. (2) into theoretical Eq. (1) of the works [9–12] and assuming that $\sigma_c \approx \sigma$, we get the equation:

$$C_n = \frac{a\gamma[A]_c}{1 + \gamma[A]_c \exp(2\sigma V_m/RTr)}, \tag{3}$$

which in the range of low concentrations $\gamma K_a[A] \rightarrow 0$ transforms into the straight line $C_n = a\gamma[A]_c$, whose slope is independent of $[Z]$ and which is the tangent for the whole set of the curves in Figure 3.

In accord with the present consideration, $[Z]$ corresponds to the "memory" volume, stored on the surface of cavities in carcass stabilized in the sponge matrix. According to the method of sample preparation the increase of cavity radius is combined with the decrease of the second component contribution in the sorption Eq. (3) denominator. This naturally explains the character of straightening the curves in Figure 3 with the increase of PNA concentration in alcohol.

SORPTION PROPERTIES OF SPONGE MICELLES

The factor of structural-entropic insensitivity of a chain sponge to the chemical nature of a sorbate is observed in a definite range in the regularities of volatile additive equilibrium sorption. The sorption picture may be presented taking into account the carcass limitation of chain spongy domain swelling and entropic solvation, specific for such domains.

Entering a chain sponge, an additive molecule strives to regulate chain units surrounding it into a capsule–micropore. Consequently, a part of chains has a decreased entropy, but the decrease is compensated by the increase of entropy of the same chain "tails". Realizing dynamically its conformational pack, chain "tails" stabilize the capsule–micropore, forming a relatively mobile fringed layer and providing spontaneous structure formation, which, represents the simplest micelle.

The situation described always accompanies the absorption of additives in any amounts due to chain flexibility. Even if the sponge is composed of hydrophobic chains, it is capable for absorbing some amount of water decreasing the Gibbs potential by the account of entropic solvation. Similar solvation also provides sorption of oleophilic non-solvents. In both cases, the sponge adapts for the structure of a microporous adsorbent, because it is in the osmotic equilibrium state.

The theory of microporous adsorbents with rigid carcass (zeolite and active coals type) states that captured molecules are localized in the volumes of narrow micropores, interacting physically with practically all atoms of solid microporous body, changing chemical potential, enthalpy and entropy of adsorbent. The change of adsorbent chemical potential is characterized by the integral:

$$\Phi = \int_0^{\mu} a d\mu,$$

which is called the Gibbs integral by Bangham [29]. Here a is the adsorption value: μ is the chemical potential; $d\mu$ is the change of the sorbed substance chemical potential. This integral is calculated from experiments and represents the main thermodynamic variable. It characterizes thermodynamic equilibrium state and is independent of physical inertness or non-inertness of the adsorbent.

It should be noted that physical non-inertness of the chain sponge in sorption is associated with its activity for adjusting to captured additive molecule. In this case the influence of introduced molecules expands to the chains of the whole sponge *via* elastic forces, and osmotic equilibrium of the system is realized at the change of the chain conformation of total sponge ensemble.

The non-inertness property of the sponge, inadequate for rigid adsorbents, requires a correction for the conclusion of the adsorptional equilibrium theory, made on the basis of thermodynamic of vacancy solutions. In accordance with the vacancy solution theory [30] the osmotic potential of a microporous adsorbent with rigid carcass equals Φ/a_m, where a_m (mol/g) is the ultimate adsorption of an additive at completely filled adsorptional volume. Osmotic pressure π of the vacancy solution is

$$\pi = \frac{\Phi}{a_m V^0} = \frac{\Phi}{W_m}, \tag{4}$$

where $W_m = a_m V^0$ is the micropore volume; V^0 is the molar volume of the adsorbate, equal to that of vacancies in the rigid microporous adsorbent structure.

Accounting of the osmotic pressure factor for the equilibrium adsorption conditions leads to the adsorption isotherm Eq. [30]:

$$a = \frac{a_m \beta P^{1/g}}{1 + \beta P^{1/g}},$$

where β is the constant; g is the osmotic coefficient accounting the non-ideality of the vacancy solution. For the ideal solution $g = 1$, and the equation obtained in [30] transforms into the Langmuir equation, which together with the Henry equation is the condition of the ideal solution in a microporous body. This equation may also respond to the sorption by ultimately rigid-chain polymer provided the vacancies accessible for adsorption are available.

With not very rigid chains, the sponge adjusts more or less actively to the molecules captured, even if it possesses no vacancies of the current size and forming filled micropores in amount, determined by forces of elastic counteraction. Swelling pressure caused by absorption is transferred from capsules of simplest micelles to their fringed surrounding and, finally, to the surface layer of spongy domains.

This process is promoted only by dispersion forces. Hence, we can present the adsorption potential (A) as a function of absorbed molecule volume [27, p. 140], *i.e.*, the function of $W = aV^0$. Neglecting the contribution of free vacancies for the osmotic equilibrium of a sponge with flexible chains, we can use the equation

$$\pi = \frac{\Phi}{W}$$

instead of the Eq. (4). Then, the adsorptional potential, *e.g.*, the work for transferring 1 mole of adsorbed additive into the equilibrium gas phase

$$A = RT\ln\left(\frac{P_s}{P}\right)$$

characterizes the work against sorptional forces. Here P and P_s are pressures of the equilibrium and saturated sorbate vapors, respectively. Definite values of a and P/P_s, which allow us to obtain the dependence of A on W, correspond to each point of the sorption isotherm $W = aV^0$.

According to [27] the function $A(W)$ does not depend on temperature because of the temperature independence of electromagnetic dispersion forces, and the equation of the volume filling of micropores theory (VFMT) must be fulfilled:

$$a = a_0 \exp\left[-\frac{A^n}{E^n}\right], \tag{5}$$

where E is the characteristic sorption energy, n is a constant. Usually, for rigid-carcass adsorbents $n > 2$ and E is high: 10–30 kJ/mol; for polymers $n < 1$ and E is low: 0.5–3 kJ/mol [28, 31].

Figure 4 shows Curve 1 of n-hexane sorption and Curve 2 of water sorption by CTA samples, calculated by Eq. (5). it also shows Curve 3 of ethylacetate sorption by cellulose acetate. Experimental points ($T = 298$ K), necessary for the curves, were taken from the works [32–34]. Parameters of Eq. (5), obtained by the method from [28, 35], equals: $a_0 = 0.9$ mol/kg, $E = 0.7$ kJ/mol and $n = 0.45$ for n-hexane; $a_0 = 0.13$ g/g, $E = 1.25$ kJ/mol and $n = 0.7$ for water; $a_0 = 0.48$ g/g, $E = 1.48$ kJ/mol and $n = 0.7$ for ethylacetate.

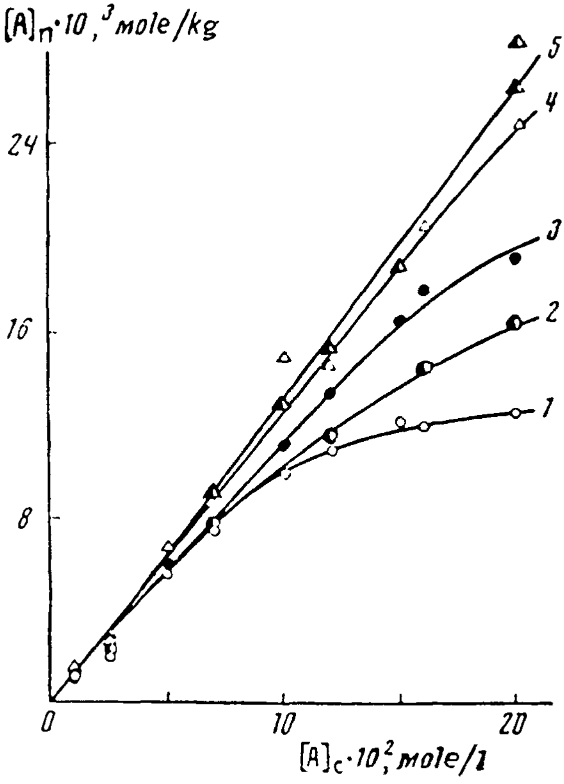

FIGURE 4 Isotherms of n-hexane (1), water (2) and ethylacetate (3) vapors sorption by CTA films (1, 2) and CA (3). Values a_1 and a_2 relate to Curves 1 and 2, respectively.

Coincidence of the calculated curves with the experimental points in Figure 4 evidences the fulfillment of the VFMT equation and proves the equal absorption mechanism of the substances which are significantly different in their physical nature. The existence of the S-form curves, low E value, and $n < 1$ reflect the action of adsorption forces in the system, in which tight micropores are formed under the effect of captured molecules, and additive molecules themselves are localized in the bulk of formed micropores with no direct interaction with one or another center on the polymeric chain (CO-groups, for example).

According to VFMT, if the sorption isotherm at a single temperature is known, one may calculate an isotherm for another temperature using more general Eq. [28]:

$$a = a_{00} \exp\left[-\left(\frac{A}{E}\right)^n - \alpha(T - T_0)\right], \tag{6}$$

where a_{00} is the ultimate sorption at temperature T_0; α is the sorption thermal coefficient.

We have checked the correspondent calculations using experimental isotherms of water sorption by PMMA films at 303 and 318 K [36] and the series of vapor sorption isotherms of PNA stabilizer by PP melt [37]. Showing no curves for PMMA, let us mention that the experiment correlates well with Eq. (6) at the values of coefficients: $E = 1.75\,\text{kJ/mol}$, $n = 0.7$, $\alpha = 0.0063\ \text{grad}^{-1}$, and $a_{00} = 0.024\,\text{g/g}$ at $T_0 = 303\,\text{K}$. Consequently, the water sorption with PMMA also proceeds by means of the introduction of molecules into the chain sponge and their localization in the volumes of created micropores without CO-group solvation. Regularities of PMMA swelling in water vapor testify the additivity of the volumes of the components and that water does not fill the existing cavities, but pushes the chains apart [36].

The data of PNA stabilizer sorption by PP melt are shown in Figure 5. For the calculation of curves in Figure 5 we used the proportion condition

$$\frac{P}{P_s} = \frac{[A]_c}{[A]_c^{\infty}}$$

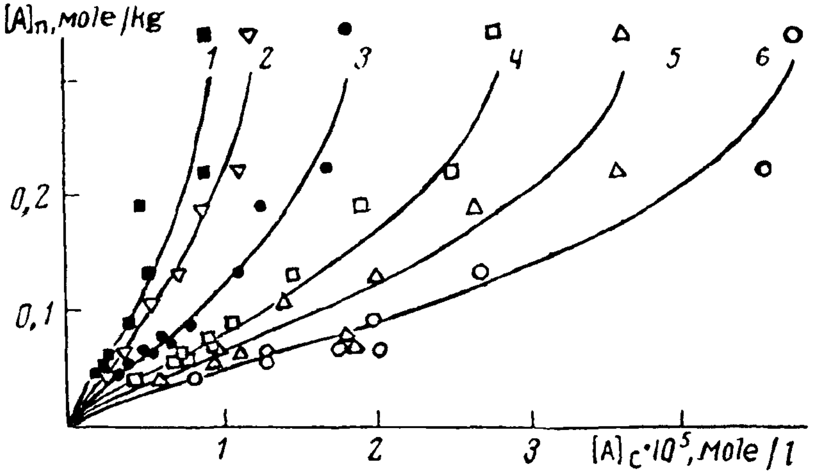

FIGURE 5 Isotherms of PNA sorption by PP melt at 160 (1), 170 (2), 180 (3), 190 (4), 200 (5) and 210°C (6).

and saturated vapor concentration $[A]_c^\infty$ determined by the last points of the curves. All the curves shown in Figure 5 (for 170, 180, 190, 200, and 210°C) are described by Eq. (6) on the basis of the curve at $T = 160°\mathrm{C}$ at the parameters $a_{00} = [A]_n^\infty = 0.27\,\mathrm{mol/kg}$, $E = 3.0\,\mathrm{kJ/mol}$, $n = 0.7$, and $\alpha = -0.001\,\mathrm{grad}^{-1}$. It is seen from Figure 5 that the correlation of the theory with the experiment takes place in the entire interval of P/P_s values. Thus, the general mechanism of PNA absorption acts in the entire range of the work conditions [37] at simultaneous fulfilling one of the main VFMT requirements, namely, the temperature invariability of the sorption work.

It should be noted that the authors of [37] failed in explaining the experimental points shown in Figure 5. They just mentioned the presence of a very narrow Langmuir initial part on the sorption curves and an apparently continuous change of the sorption mechanism owing to the structural changes proceeding in the polymer above the Langmuir part of curves.

It should be also noted that in works on rigid-carcass adsorbents, the technique of adsorption heat determination by the initial parts of curves is often used, approximating them by the Henry equation. Applying such method, the authors of [9–11] have found positive heat effects (negative ΔH_s) valued as 43 – 54 and 45 – 58 kJ/mol for the absorption of diphenylamine and phenylbenzoate by solid PP films. The same limits rounded the heat value that we calculated for water sorption by PMMA from the data of [36]. The results of such calculations were one of the reasons for the development of the model of rigid center sorption [9 – 12]. At the same time, the consideration performed testifies the invalidity of the latter model in relation to polymers and, consequently, different physical sense of the ΔH_s value.

The approximation of the initial part of sorption isotherm by the Henry equation definitely changes indexes n and RT/E by 1, transforming thus, the Eq. (5) as follows:

$$a = a_0 \exp\left[-\left(\frac{A}{E}\right)^n\right] \to a_0 \exp\left[RT\frac{\ln(P/P_s)}{E}\right] \to$$

$$\to a_0 \exp\left[\ln\left(\frac{P}{P_s}\right)\right] = a\left(\frac{P}{P_s}\right) = K_s P.$$

The apparent sorption constant $K_s = (a_0/P_s)$, calculated in this way, includes the pressure of saturated vapors, which is characterized by the exponential dependence on temperature in a wide temperature range [15, p. 144]:

$$P_s = B \exp\left(-\frac{\lambda}{RT}\right),$$

where B is a constant; λ is the evaporation heat (sublimation). Thus, the heat calculated by the Henry formula (K_h = const $\exp[-(\Delta H_s/RT)]$) from the "constant" $K_s = (a_0/B)\exp(\lambda/RT)$ obtains the effective positive valued, $\Delta H_s = -\lambda$.

With the observed parameters n and E the apparent value ΔH_s represents, in reality, a signal of the sponge as a peculiar probe for the internal influence at the osmotic equilibrium with the phase of the gaseous sorbate.

CONCLUSION

We can conclude that the concept of the polymeric micellar spongous structure forms the basis for the general approach describing the mechanisms of polymers mixing with low-molecular compounds, competition of additives for a place in the sponge and sorption. The account of entropy-solvational properties of spongous micelles allows us to use fundamental concepts of the theories, developed for rigid-carcass microporous adsorbents. In this case, high efficiency of VFMT was calculated for the description of absorption by glassy, highly elastic and molten polymers.

It should be specially noted that the flexibility of chains polymers requires an accurate application of adsorption theories, which use the concept of filling in layers of internal cavities surfaces. For example, this is bound to the isotherm of *n*-hexane sorption by CTA films (Fig. 4, Curve 1), shown in the manual [32] as an illustration of local center filling by condensation of molecules in layers.

The study of the polymer-chain sponge properties is also important for the process of "washing" with water of technological additives of stabilizers and plasticizers, and drug forms specially introduced into polymers. As it became understandable, water introduced into a sponge due to osmosis at rather high vapor activity decreases solubility of oleophils by the mechanism of structural-entropic solvation even in the absence of hydrophilic additives in the polymers. Thus it stimulates exudation of the additives.

It should be also noted that validity of the VFMT equation was shown before on the examples of water sorption by fibers of viscose, cotton, caprone, polyvinyl alcohol, polyacrylonitryl [28], and sorption of sulfurous gas by glassy and highly elastic polysiloxanes [31]. However, these works were not aimed at the disclosure of the physical nature of the sorption mechanism, determined by the chain sponge properties. It was shown in the present article, however, it was shown that this mechanism corresponds to the synthesis of a microporous sorbent under the effect of osmosis.

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