Sponge Effects in Polymers Interacting with Low-Molecular Weight Compounds

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ABSTRACT: The competition between additives for a place in the polymer matrix are discovered when the blending components ensure the enthalpy of mixing to be nearly zero. The competition of the additives exists as the process of accelerated exudation of one another from glasslike or jellylike films. This is inconsistent with the entropic nature of the mixtures assumed for the homogeneous polymer solutions. The considered effects are beyond the statistical thermodynamics of solutions, and they are explained by the specificity of the chain-sponge organization of a noncrystalline polymer matrix. The equilibrium sorption of volatile compounds by polymer samples is explained by the mechanism of structural entropic solvation and is described by the equation of the micropore volume filling theory. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 2435–2442, 2000

Key words: sponge structure; liquid; miscibility; volatile compound; sorption

INTRODUCTION

It is common knowledge that some properties of highly elastic and melted polymers are explained by the statistical thermodynamics of flexible polymer chains.[1] Progress in this field induced consequent attempts to transfer liquid-phase notions to glasslike and jellylike systems. However, the structural model manifesting a polymer as a high-molecular weight liquid is inadequate for the polymer objects that display a supermolecular skeleton composed of polymer chains packed as a spongy body. The existence of a supermolecular spongy skeleton is thought to be responsible for the invalidity of the homogeneous statistics in explaining, for example, the cold flow, memory effects, and non-Newton flow of melts[2]; plasticization anomalies, antiplasticization, and properties of jellies[3,4]; sorption,[5] the phenomenon of thermodynamic affinity splitting in the single

"polymer–liquid nonsolvent" pair,[6] important kinetic features of free radical chain reactions,[7] and peculiarities of exothermic effects when mixing polymers with their hydrogenized monomers.[8,9]

The present article contains data on the responsibility of the chain sponge for the processes of interaction with low-molecular weight compounds, which are anomalies from the liquid-phase thermodynamics point of view.

EXPERIMENTAL

Optically transparent noncrystalline films of poly(methylmethacrylate) (PMMA) with a number average molecular weight (M_n) of 140,000 and cellulose triacetate (CTA) with a volume average $M(M_v)$ of 330,000 were used. They contained different amounts of spectrally pure additives of two aromatic compounds: the liquid plasticizer dibutylphthalate (DBP, $T_{boil} = 340°C$) and naphthalene ($T_{boil} = 80.2°C$). Films (10–50 μm thick) were prepared from the components dissolved in methylene chloride (MC) and chloroform

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by vaporizing solvents in Petri dishes. All the compounds used are characterized in the literature by a close solubility index δ (J/mL)$^{0.5}$: polymers, 19.0; methylene chloride, 19.86; chloroform, 19.0; DBP, 19.8; naphthalene, 20.4. (In accordance with the literature,[10] δ for naphthalene is accepted as the same as nitrobenzene.) Spectrally pure heptane ($\delta = 15.3$) and distilled water ($\delta = 46.4$) were also used.[11] Spontaneous and stimulated desorptions of additives were studied via the change of their UV absorption with a Specord UV-vis device. Diffusion coefficients D_d were calculated from the linear plots of the admixture optical density D change 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 corresponded to the maxima of the absorption bands of 34,400 or 32,200 cm^{-1} for naphthalene and 36,600 cm^{-1} for DBP. The DBP release from the films with its high concentration was calculated by the following 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, and t is the current time.

Desorption of naphthalene possesses an initial period during which the process rate is extremely low. When heating CTA films with 1% naphthalene in air, this period may reach 100 min; but it decreases simultaneously with the increase of concentration, in the presence of DBP, and when heating the films in water. The reason for the delay in the initial stages of the diffusion process is thought to be the formation of relatively rigid surface crusts with decreased entropy of a polymer-chain sponge when evaporating the solvent. This phenomenon implies a decrease of the admixture solubility, promoting the additive to migrate from surface layers into the depth of the film. The apparent layer inhomogeneity is fixed as a result of drying and vitrification of the samples. Thus, transition of the desorption process into the stationary diffusion stage requires definite time.

RESULTS AND DISCUSSION

According to statistical thermodynamics, the equality of solubility indexes excludes the role of the enthalpic factor in mixing of liquids and the spontaneous mixing is induced by an increase of the entropy of the homogeneous solution. A mixture formed from a pair of such components is not affected by the third added component that possesses the same solubility index. Because it possesses no preferable interaction with another component, the third one cannot decrease their affinity to increase the total entropy of the homogeneous mixture. Concerning the water effect on the binary homogeneous mixture of oleophils, there are also no reasons for their separation, because water is actively detached from the hydrophobic mixture. However, experiments prove the antagonism among the different oleophils, which occupied a polymer spongy matrix, and the water-stimulated desorption of oleophils from hydrophobic polymers.

Exudation Effects Induced by Intrastructural Oleophilic Additive

Interesting processes were already observed in the preparation of films with DBP and naphthalene. Equilibrium sorption of these compounds by CTA and PMMA films reaches only several percent at room temperature, 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 jellies with 90% DBP are insoluble in an excess of liquid DBP, even at 100°C.[6]

Glasslike CTA and PMMA films, which contain one of the above-mentioned compounds, release an additive extremely slowly and preserve its initial amount during periods of weeks and months. One should also expect equal stability of the films that contain two additives that possess nearly equal solubility indexes because of the absence of energetic interaction and competition for any sorption centers. However, one may succeed in introducing only 5% naphthalene into CTA films if the concentration of simultaneously introduced DBP does not exceed 15%. If the DBP concentration is 20%, most of the naphthalene escapes during the film formation.

The process of naphthalene escape from CTA and PMMA films formed with 30% DBP was studied in more detail. Solutions were prepared with 5.5% naphthalene per dry residue. In this case, the solvent was evaporated in open Petri cups from a 0.8 mm thick layer of the solution. Glasslike films of 45-μm thickness were obtained after 1 or 2 h, and 1 day after the naphthalene concentration in them was only 2% of the initial amount.
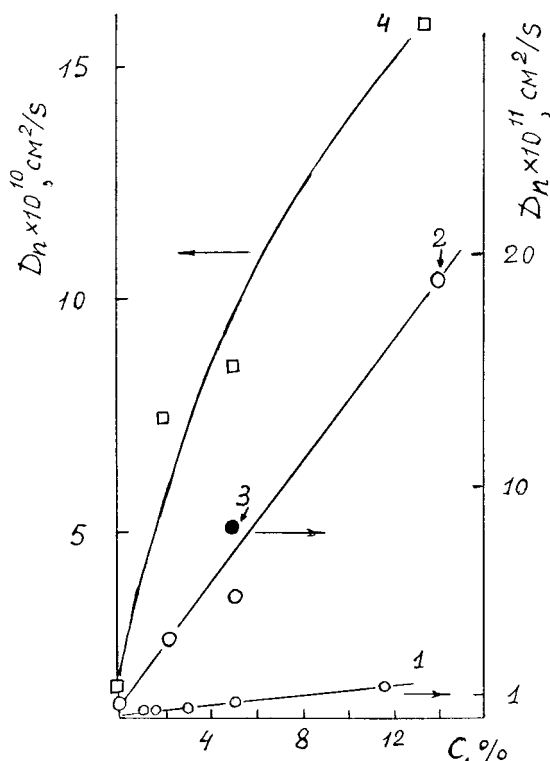
Figure 1 The coefficient of naphthalene diffusion from CTA films with naphthalene only (curve 1) and CTA films with DBP and 5% naphthalene (curves 2–4) versus the concentration of naphthalene (curve 1) and DBP (curves 2–4) when diffusing in air (curves 1, 2), liquid DBP (curve 3), and water (4) at 99 (curves 1–3) and 80°C (curve 4).

At the same time, after the free naphthalene evaporation from the liquid layer of the DBP solution, the naphthalene residue showed 3% of its initial amount for the same conditions. So the rate of naphthalene evaporation from glassy films containing DBP was not lower than from liquid DBP whereas in the absence of DBP the loss was not observed during either MC evaporation or long-term storage of the films with a naphthalene concentration of up to 20%.

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

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

and curve 2 shows it for the DBP concentration C_D (%) for $C_n = 5\%$:

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

Thus, DBP added to the CTA films causes a 10-fold higher effect on desorption than naphthalene only.

The observed effect may be formally related to the plasticization effect. However, it is characterized by the process proceeding in glasslike films. Moreover, the D_n constants of desorption in air and in liquid DBP heated to 99°C (Fig. 1, point 3) are practically equal. Consequently, in this case we may consider the structural-heterogeneous plasticization of the type observed previously[12] according to an increase of the isomerization rate of benzospyranic dyes on glasslike PMMA. Despite the intrinsic rigidity of the glass samples, the isomerization rate increased to its liquid-phase values in the presence of a small amount of additive plasticizers.

The physical sense of such intrastructural plasticization may be bound to the autonomous activation of dynamics of the chain-sponge domains being capsulated in the cells of a rigid paracrystalline carcass that is insoluble in DBP, even at 99°C.

Elimination Effects Induced by External Nonsolvents

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

The experiments showed that the coefficient of DBP diffusion (D_D) from CTA films into heptane at 95°C increased with the DBP concentration: 2.0×10^{-12}, 8.0×10^{-11}, and 1.0×10^{-9} cm^2/s for $C_D = 1.4$, 14.0, and 55.0%, respectively. Desorption from the films with 19% DBP in air gave a low D_D of 7.0×10^{-13} cm^2/s. It was practically not observed at 1.4% during 50 h, but in heptane the plasticizer extrusion from the films with a $C_D > 50\%$ was completed in only 1.5 h.

In addition, the films with a $C_D > 50\%$ retained the initial thickness and volume, thereby demonstrating a bypass in blending the external

nonsolvent with the polymer, whose spongy system is kept swollen because of the heptane osmotic pressure. The amount of absorbed heptane reached 6 mol/kg and significantly exceeded the equilibrium sorption by the pure polymer films.

The experiment with heptane proved the formation of a microporous adsorbent structure in polymeric chain-sponge domains. It was cemented more or less rigidly by domains of the paracrystalline carcass composed during solvent evaporation. The current conditions of the carcass self-assemblage affected the final mechanical force balance between the spongy domains and those of the paracrystalline carcass in the polymer body that was expressed, for example, in the values of the above-mentioned coefficient D_D. Thus, sufficient skeleton rigidity was the factor that preserved the microporosity of the CTA samples during the DBP exudation and following evaporation of heptane.

In addition, we should mention some known facts related to the chain-sponge structure of polymers. For example, data[13] revealed the effect of additive filler (stylbene) on the equilibrium sorption of benzophenon (vapors, 30°C) by glasslike polycarbonate (PC) films. Stylbene significantly increased the amount of benzophenon absorbed, but it was simultaneously completely exuded from the films. Thus, stylbene stabilizes the sponge structure of the PC matrix and provides an increased sorption bypass for the blending of benzophenon with PC by imparting the occupied places for benzophenon molecules, similar to DBP substitution by heptane in CTA films.

There was also another case that evidenced the bypass combination of poly(vinyl chloride) (PVC) with alcohols as nonsolvents.[14] Large amounts of methanol, ethanol, n-propanol, isopropanol, butanol, isobutanol, and 2-ethylhexanol accumulated in the polymer matrix during exudation of DBP or dioctylphthalate, which was preliminarily introduced into the polymer by the action of the liquids on the plasticized films.

The structural similarity of plasticized and glasslike polymers filled with additives to microporous sorbents was obtained by the NMR technique[15] and electron spin resonance probation.[16] 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.[17,18] However, in the cited works a conclusion about the chain-sponge carcass-micellar structure was not formulated. At the present time the properties of the molecular sponge are rather clear.[6,7,9,19,20]

Elimination Effects Induced by Water

Sorption equilibrium of water with pure CTA and PMMA films reached 11 and 2.3%, respectively, at $P/P_s = 1$, but it decreased 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, it is believed, from the liquid-phase thermodynamics point of view, that water influence on the composition of two- or three-component homogeneous mixtures of oleophils will not stimulate separation of the components. However, water eliminates DBP from the glasslike and jellylike films of both polymers. Escaped plasticizer covered the film surface with small drops and increased the UV optical density by means of light losses for refraction. Those drops were removed by filter paper during the experiment.

At 95°C the water was able to extrude DBP completely from glasslike and jellylike films. The process in jellies was accompanied by a significant decrease of the thickness (and volume) of the samples (by 2–3 times), so polymer chains in the resulting samples were packed as in usual glasslike films. The effective coefficients of DBP diffusion calculated for the initial film thickness did not depend on the plasticizer concentration and gave $(2 \pm 1) \times 10^{-11}$ cm^2/s at $C_d = 1.4, 19, 43, 65,$ and 86%. Thus, in accordance with the diffusion constants, the efficiency of external eliminator was inverted: at $C_d = 1.4\%$ the water was much more active than heptane, and at 14% and higher the heptane became more active than water.

The difference between water and heptane is connected not only with values of the D_d coefficients, but also with mechanical work to squeeze and make the polymer chain packing dense. The osmotic pressure of heptane acts in a way to preserve the microporosity, which is prepreserved by a plasticizer, when providing stimulated DBP extrusion. On the contrary, the osmotic pressure of water provides the process of isothermal matrix compression. Both these situations, in their physical sense, are out of the frame of statistical thermodynamics and do not conform with the ideas about the components' competition for structurally stationary sorption centers.

Water also accelerates naphthalene desorption. At 99°C it affected CTA films with 1% of

naphthalene stronger than heptane to make the D_n coefficient 3×10^{-10} versus 1×10^{-11} cm²/s in heptane (1×10^{-12} cm²/s in air). At the concentration of 11.4%, desorption in water showed a diffusion coefficient of 1.5×10^{-9} versus 1.6×10^{-11} cm²/s in air.

An increase of hydrophobicity of CTA films with 5% naphthalene through the introduction of 5% DBP significantly increased the water influence. This is shown in Figure 1 (curve 4) for the hydrostimulated process at 80°C. Curve 4 lies above 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 (100s and 1000s of times stronger) does not match the properties of the homogeneous oleophil solution.

According to the homogeneous-statistic definition, the role of the enthalpic factor is excluded in the mixtures of oleophils used, but it is very important for their interaction with water, because a very high δ value of water leads to a significant endothermic effect of its mixing with fats. Neither the homogeneous solution theory nor the concept of stationary centers of absorption is able to explain the reason for stimulated elimination of any oleophil by water. In postulates this phenomenon is thought to increase the free energy (the Gibbs potential), which contradicts thermodynamic principles.

The scenario described can be connected to the effect of a sponge under the osmotic pressure of water. The primary polymer chain sponge contains an oleophil, whose molecules are weakly linked to the surrounding segments. The quasiequilibrium state of additive molecules in the sponge is kept steady by the osmotic equilibrium with vapors of the additive above the film and also by means of the structural reorganization of sponge-chain units surrounding each one of the additive molecules. The reorganization is determined by the conformational changes of sponge chains that provides a definite increase of the entropy. Because it possesses such properties, the sponge is somewhat indifferent to the chemical composition of captured molecules. Thus, the action of water is caused by the high activity of its vapors above the films.

The relative indifference of the sponge to the chemical nature of captured additives was also shown by hydrostimulated desorption of hydrophilic compounds. For example, the active water extrusion of hydrogen peroxide from the samples of PMMA swollen in H_2O_2 was observed by Her-

man and Giguere.[21] Hydrogen peroxide possesses a solubility index of 45.2 (J/mL)$^{0.5}$, which is practically equal to that of water, and mixes with water at any ratio. According to their data,[21] spontaneous desorption of water and hydrogen peroxide from PMMA films in air possesses diffusion coefficients of 3 and 9×10^{-8} cm²/min, respectively. Hydrogen peroxide plasticizes the polymer, which is why it possesses a higher diffusion coefficient; but a much higher coefficient of 3.5×10^{-4} cm²/min was found for the peroxide desorption from films placed in water.

Sorption Properties of Polymer Sponge Micelles

The foregoing sections indicated that the structural–entropic properties of a chain sponge, which are insensitive to the chemical nature of a sorbate, were the main factor ensuring the sorption of volatile additives. The sorption picture may be understood by taking into account the carcass limitation of the chain-spongy domain swelling and entropic solvation specific for such domains.

When entering a chain sponge, an additive molecule is thought to impart the pressure to chain units surrounding it, arranging the units into a capsule–micropore. Consequently, a part of the chain links lose entropy, but this is compensated by the increase of entropy of the "tail" links of the same chains. Dynamically realizing its conformational pack, the chain sponge stabilizes the capsule–micropore as a nucleus surrounded by a relatively mobile fringed layer and thereby provides spontaneous structure formation that, in fact, is the simplest micelle.

The situation described always accompanies the absorption of some amount of additives, which is due to chain flexibility. Even if the sponge is composed of hydrophobic chains, it is capable of absorbing some amount of water and decreasing the Gibbs potential under the entropic solvation. A similar solvation also provides sorption of nonsolvent oleophils. In both cases, being in the osmotic equilibrium state, the sponge transforms itself to the structure of a microporous adsorbent.

The theory of microporous adsorbents with rigid carcasses (zeolite and active coals types) declares that captured molecules are localized in the volumes of narrow micropores and interact physically with practically all atoms of the microporous body and change the chemical potential, enthalpy, and entropy of the adsorbent. The

2440   MIKHEEV, GUSEVA, AND ZAIKOV

change of adsorbent chemical potential is characterized by the integral[22]

$$-\Delta\mu_{abs} = \Phi = \int_{P=0}^{P} (n_1/n_a)RT \, lnP.$$

Here n_1 and n_a are the mol values of the sorbed substance and the adsorbent, respectively; and P is the equilibrium vapor pressure. This integral is calculated from experiments and represents the main thermodynamic variable. It characterizes the thermodynamic equilibrium state and is bound to no hypothesis on the physical inertness or noninertness of the adsorbent.

It should be noted that the physical noninertness of the chain sponge in sorption appears in its ability to adjust itself to the captured additive molecule. In this case the influence of introduced molecules expands to the chains of the whole sponge through elastic forces, and osmotic equilibrium of the system is realized at the change of the chain conformation of the total spongy ensemble.

Because it possesses flexible chains, the sponge adjusts more or less actively to the molecules captured, even if it possesses no vacancies of matching size. Swelling pressure caused by absorption is transferred from the capsules of the simplest micelles to their fringes and finally to the surface layer of spongy grains.

This process, making no match for the vacancy solution theory,[23] is promoted only by dispersion forces that allow the presentation of the adsorption potential (A) as a function of the absorbed molecule volume[24] (i.e., the function of $W = aV^0$, here V^0 is simultaneously the molar volume of the real solvent, i.e., the sponge emptiness). Neglecting the contribution of free vacancies for the osmotic equilibrium of a sponge with flexible chains, one should take the equation[1]

$$\pi_{swell} = \frac{\Phi}{V^0},$$

actual by the small degree of the polymer swelling. The adsorption potential (i.e., the work for transferring 1 mol of adsorbed additive into the equilibrium gas phase)

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

characterizes the work against sorption forces. Here P and P_s are the pressures of the nonsaturated and saturated equilibrium 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 $W = aV^0$.

It is also agreed[24] that the function $A(W)$ does not depend on the temperature as a result of the temperature independence of electromagnetic dispersion forces, and the equation of the volume filling of micropores theory (VFMT) must be fulfilled:

$$a = a_0\exp\left[-\frac{A^n}{E^n}\right], \qquad (1)$$

where E is the characteristic sorption energy and 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).[25,26]

Figure 2 shows the n-hexane sorption (curve 1) and water sorption (curve 2) by CTA samples, which were calculated by eq. (1). It also shows ethylacetate sorption (curve 3) by cellulose acetate. Experimental points ($T = 298$ K), which are necessary for the curves, were taken from several works.[27–29] The parameters of eq. (1) were obtained by a literature method[25,30]: $a_0 = 0.9$ 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.

The coincidence of the calculated curves with the experimental points in Figure 2 indicates the fulfillment of the VFMT equation and proves the equal mechanism of absorption of the substances that are significantly different in their physical nature. Thus, the sorption isotherm calculations indicate that the tight micropores are formed under the captured molecules that are localized in the bulk of formed micropores that are in no direct interaction with another center on the polymeric chain (e.g., CO groups).

According to VFMT, if the sorption isotherm at a temperature T_0 is known, one may calculate an isotherm for another temperature using the following more general equation[25]:

$$a = a_{00}\exp\left[-\left(\frac{A}{E}\right)^n - \alpha(T - T_0)\right], \qquad (2)$$

where a_{00} is the ultimate sorption at temperature T_0 and α is the sorption thermal coefficient.
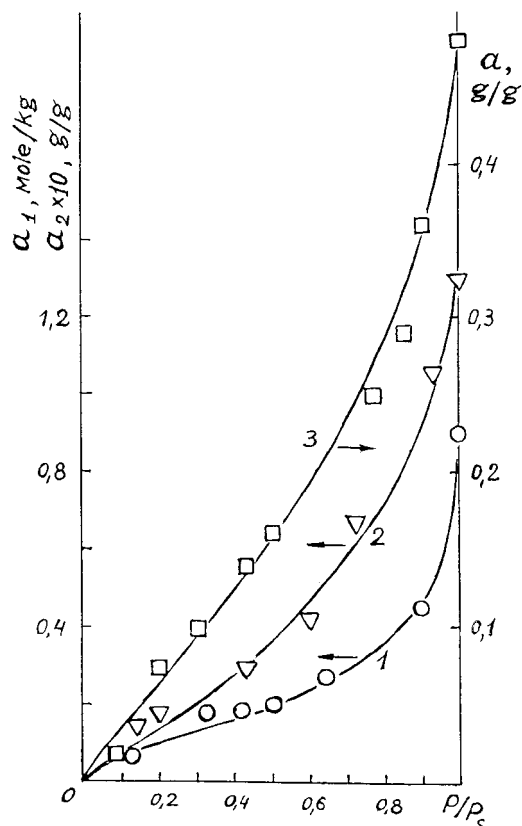
Figure 2 Isotherms of n-hexane (curve 1), water (curve 2), and ethylacetate (curve 3) vapor sorption by CTA films (curves 1, 2) and CA (curve 3). The values of a_1 and a_2 relate to curves 1 and 2, respectively.

We checked the correspondent calculations using experimental isotherms of water sorption by PMMA films[31] at 303 and 318 K and the series of vapor sorption isotherms of the stabilizer phenyl-β-naphthyl-amine (PNA) by a polypropylene (PP) melt.[32] Showing no curves for PMMA, let us mention that the experiment correlates well with eq. (2) at the coefficient values of $E = 1.75$ kJ/mol, $n = 0.7$, $\alpha = 0.0063$ grad^{-1}, and $a_{00} = 0.024$ g/g at $T_0 = 303$ K. Thus, water sorption by 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 hydration. In agreement with VFMT, regularities of PMMA swelling in water vapor indicate the additivity of the volumes of the components and the absorbed water molecules do not fill the existing cavities, instead strictly pushing the chains.[31]

The data on PNA stabilizer sorption by a PP melt are shown in Figure 3. For the calculation of curves in Figure 3 we used the proportion condition

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

and saturated vapor concentration $[A]_c^\infty$ determined by the last points of the curves. All the curves shown in Figure 3 (for 160, 170, 180, 190, 200, and 210°C) are described by eq. (2) on the basis of the curve at a T_0 of 160°C at the parameters $a_{00} = [A]_n^\infty = 0.27$ mol/kg, $E = 3.0$ kJ/mol, $n = 0.7$, and $\alpha = -0.001$ grad^{-1}. Note from Figure 3 that correlation of the theory with the experiment takes place on the whole interval of P/P_s values. Thus, the general mechanism of PNA absorption acts in the whole range of the work conditions[32] simultaneously fulfilling one of the main VFMT requirements, namely, the temperature invariability of the sorption work.

It should be noted that one group[32] could not explain the experimental points shown in Figure 3. They just mentioned the presence of very narrow Langmuir sections in the initial parts of the sorption curves and assumed continuous change of the sorption mechanism as a result of any structural changes proceeding up the Langmuir part of the curves in the polymer.

CONCLUSION

The concept of a polymeric micellar spongy structure formed the basis for the general approach to the mechanisms of polymers mixing with low-molecular weight compounds, competition of additives for a place in the sponge, and sorption. The concept of the entropy–solvational properties of
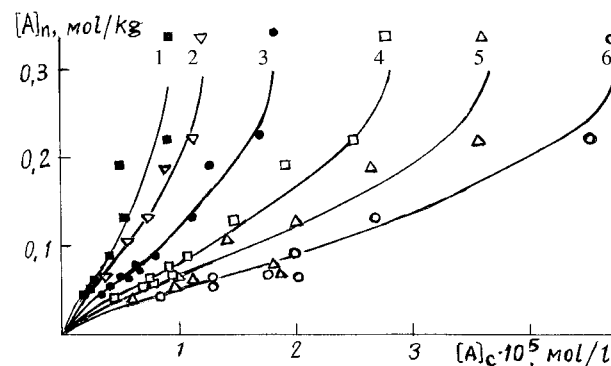
Figure 3 Isotherms of PNA sorption by the PP melt at 160 (curve 1), 170 (curve 2), 180 (curve 3), 190 (curve 4), 200 (curve 5), and 210°C (curve 6). Here $[A]_c$ and $[A]_n$ are the PNA concentration in the vapor phase and PP melt, respectively.

spongy micelles allowed us to use fundamentals developed for rigid carcass microporous adsorbents. Indeed, the high efficiency of VFMT was demonstrated for the description of absorption by glasslike, highly elastic, and melted polymers.

It should be noted that the validity of the VFMT equation was shown before in the examples of water sorption by fibers of viscose, cotton, caprone, polyvinyl alcohol, and polyacrylonitryl,[25] and sorption of sulfurous gas by glasslike and highly elastic polysiloxanes.[26] However, these works did not seek to the disclose the physical nature of the sorption mechanism that is directed by the polymer chain sponge. It was shown in the present article that this mechanism does correspond to the synthesis of a microporous sorbent directly under the osmosis.

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