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The Entropic Mechanism of Water Solvation of Polymers

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Computational analysis of isotherms of equilibrium water absorption by polymers indicates the isotherms follow the theory of volume-centered filling of micropores regardless of the hydrophilicity of polymers. Structure of a microporous adsorbent, absent in the initial state, is formed through reorganization of chains of the molecular-chain sponge during adsorption. Thus, a part of chain units is combined in micropores isolating water molecules as clusters, and another part is redistributed around the clusters as a fringe that stabilizes the system by increasing the configuration entropy.

The problem of the physical state of sorbed water in polymers is important from positions of the mechanisms of its diffusion in polymeric membranes, its effect on physical properties of polymers, participation in dyeing and fading of fabrics, superseding of stabilizers and plasticizers, and also in guided delivering of drugs in the organism from polymeric units of medical use.

Keywords: Water absorption; polymers; isotherms; micropores; molecular-chain sponge

INTRODUCTION

The following forms of water distribution in a matrix were considered regarding the water absorbed by polymers [1–3].

1. Homogeneous solution of molecules dispersed between chains;
2. Clusters combined of relatively small number of molecules;

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3. Hydrate layers around functional or non-functional (for example, formed by oxidative aging) polar groups;
4. Hydrate layers immobilized on additives.

It is postulated that in consequence of the relative vapour pressure (P/P_s) one or another form of sorbed water prevails.

Polymers able to absorb up to 1–2 weight% of water belong to hydrophobic ones, from 2 to 10% to moderate hydrophilic ones, over 10% to hydrophilic ones [1–3]. Polyolefines, fluoroplasts, rubbers, polyesters, PVC belong to the first group of polymers. The amount of water sorbed by them usually depends on the method of preparation of samples, presence of additives and existence of oxidized groups on polymer chains (for example, $-\text{COOH}$, $-\text{OH}$, $-\text{CO}-$).

Isotherms of water sorption by hydrophobic polymers is usually approximated by straight lines or by a positive deviation from them. To illustrate the mentioned properties curves for high density PE (HDPE) (curve 1), low density PE (LDPE) (curve 2), ethylene copolymer with vinylacetate (curve 3), fluoropolymer F-32 (curve 4) are shown in Figure 1 [2]. Sometimes isotherms of rubbers (Fig. 2, curves 1–4)

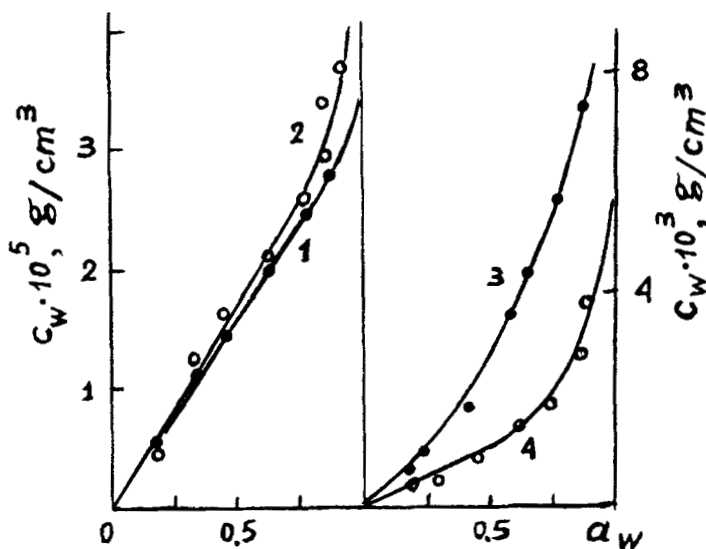


FIGURE 1 Water absorption isotherms for the hydrophobic polymers [2]: high density polyethylene (1), low density polyethylene (2), copolymer of ethylene with vinylacetate (3), fluoropolymer F-32 (4).

display a “Langmuir” part in the range of low relative vapour pressure, noticeable in natural rubbers (NR) (Fig. 2, curve 3) and specially clear in NR treated by a shallow oxidation (Fig. 2, curve 4) [4].

The existence of linear parts on isotherms (Fig. 1, curves 1–3; Fig. 2, curves 1, 2) has been attributed to molecular distribution of water between hydrophobic chains [1–3], or to hydration of polar additives and non-functional oxygen-containing groups [4]. It was proposed [4] that the hydration is confirmed by a negative apparent enthalpy of the sorption calculated by Henry’s law ($\Delta H_s = -31, -38$ kJ/mol), and also by an increase of absorption in consequence of shallow NR oxidation.

An influence of the polar groups on water sorption is much stronger in hydrophilic polymers. In this case, the energetic interaction is postulated as a reason for the appearance of the Langmuir part which leads to an *S*-like form to isotherms, and the *S*-shaped form is

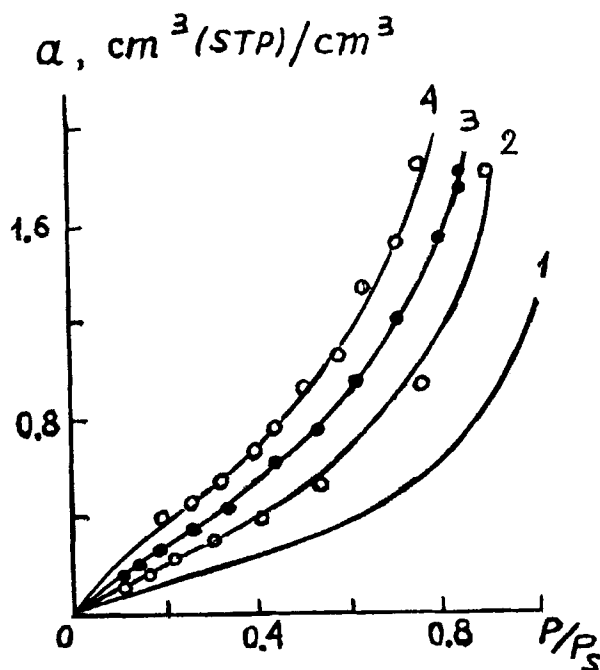


FIGURE 2 Isotherms of water absorption by the hydrophobic films of polyisoprenes [4]: Cariflex IR 305 (1), Natsyn 2200 (2), Natural rubber (3), and Natural rubber after weak oxidation. Temperature of water absorption: 36,6°C (1), 50°C (2–4).

considered as a proof of the principal difference in absorption mechanisms of hydrophilic and hydrophobic polymers. The different behavior of these polymers is presented is shown in Figure 3 (curves 1, 2, 3 corresponding to hydrophilic collagen, PVA and keratin, respectively, and curves 4 and 5 to less hydrophilic cellulose acetate (CA) and nylon-6,6 respectively).

To describe the complete isotherms, the models of so-called "bimodal" sorption are used in the literature. The essence of these models lies in joining the Henry or Langmuir equation to statistical theories of polymeric solutions [5] or clusterization of water [1-3]. However, all these approaches are inadequate for the mechanism of absorption of a low-molecular weight compound (LMC). The model based on the idea of homogeneous mixture of a polymer and LMC, for example, requires free exchange of places of LMC molecules and sponge chains, which is excluded by a rigid fixation of sponge granules in cells of the supermolecular paracrystalline carcass [6-9].

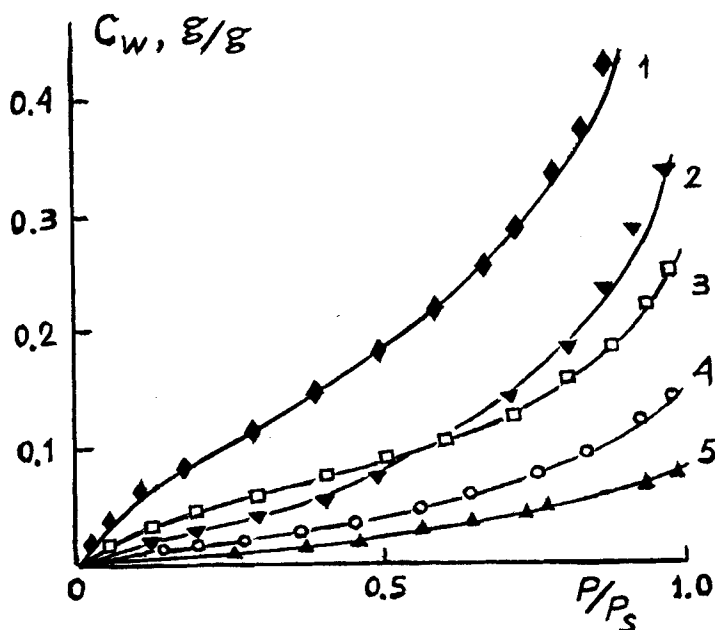


FIGURE 3 Water absorption isotherms of (hydrophilic) collagen (1), poly(vinylalcohol) (2), keratin (3), and (moderately hydrophilic) cellulose acetate (4), Nylon-6,6 (5), [2].

It is substantial that the interpretation of the Henry law and Langmuir equation, assumed for polymers, gives no explanation of the typical difference of negative sorption enthalpies ΔH_s , calculated in consequence of the Henry law, from positive isosteric enthalpies ΔH_a , calculated from the measured absorption values. As an example it can be presented that according to the work [4] these characteristics for synthetic rubbers on the same initial parts of sorption curves equal -31 and -38 kJ/mol instead of 12.1 and 4.6 kJ/mol, respectively. However, according to the theories of LMC sorption on active centers these characteristics must possess equal signs differing only by values (the point is that the Henry law assumes for sorbed molecules presence of the activity coefficient equal to 1, but the latter changes as the centers are filled. This becomes the reason for the observed inequality between ΔH_s and ΔH_a [10]).

Figure 4 shows an interesting example of changes of the isotherms of water sorption by copolymer of maleic anhydride with vinylacetate

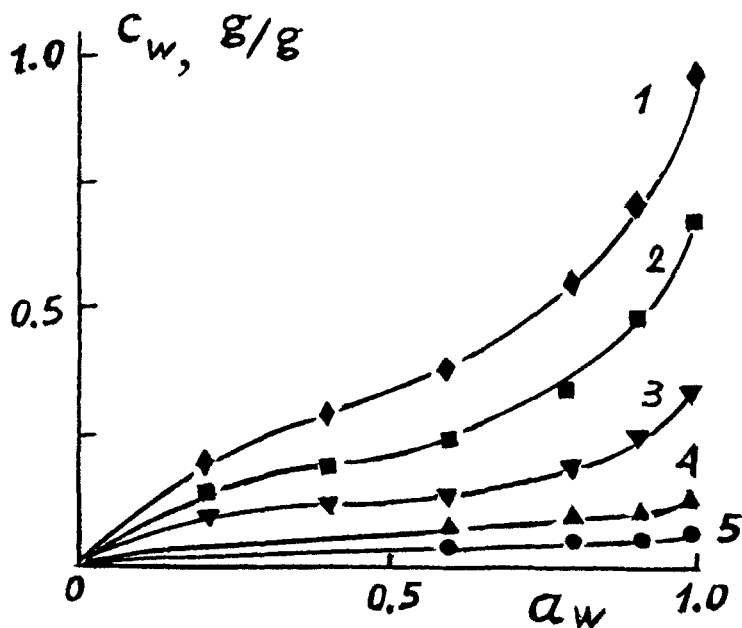


FIGURE 4 Isotherms for the absorption of water by a MAN-Vac copolymer (1) and its residues after thermal degradation at 10 (2), 20 (3), 30 (4), and 40 (5) minutes [3].

(MAN-VAc), reported in [3]. This change accompanies thermal ageing, during which soluble MAN = Vac transforms, at first, into a swollen insoluble hydrogel, and then into a hydrophobic polymer.

As it is seen from Figure 4, the change of absorption ($C_w = a$) in the range of the lowest and the highest values of P/P_s takes place in practically equal proportions. This is in poor agreement with the models predicting principally different methods of water distribution in the mentioned ranges. An increase of length of the "Langmuir" part, observed during thermal ageing, and a decrease of absorption in the zone of clusterization (high P/P_s) could reflect the increase of the role of energetic linking of water to polar centers. However, the shallow thermal ageing of a polymer, initially filled by hydrophilic groups (for example, on the stage of hydrogels, Fig. 4, curves 1–3), will hardly depend on their content and the amount of intermolecular crosslinks. Hence, in the case of real energetic linking of water, the length of the "Langmuir" part would be increased with a small decrease of its height in relation to a decrease of absorption in the range of $P/P_s \approx 1$.

This background shows the problems of reported concepts relative to the mechanism of water absorption by polymers.

RESULTS AND DISCUSSION

Absorption Isotherm as a Probe Signal of a Sponge

New ideas of the mechanism of low-molecular weight compounds (LMC) absorption by polymers were recently developed. Of special interest is the concept of the entropy factor of a non-combinatorial origin [6–9]. These ideas originate in the carcass-micellar structural model which includes two main structures: a continuous spatial carcass, aggregated from paracrystalline domains, and molecular-chain micelles with a spongy skeleton which fill cells of the paracrystalline carcass [11, 12].

The attachment of sponge chains to domains of the paracrystalline carcass eliminates the free exchange of positions between LMC molecules and chain units. Entering the sponge, an admixture molecule regulates the surrounding chain links of the capsule structure by means

of dispersion forces [8]. The ordering of chain links reduces the chain entropy, but this reduction is overcome by an increase of the entropy of "tails" of the same chains organized as a fringe layer.

After reading the complete set of their conformational states, the "tails" stabilize the formed capsule-micropore. This state is accompanied by absorption of LMC stipulated by the flexibility of chains. To decrease its excessive surface energy, such simplest micelles must coalesce forming LMC clusters.

The sorptional equilibrium is reached when the balance between vapour pressure of sorbate on the sponge and elastic tension of the sponge chains is established. These force balance is independent of hydrophilic or hydrophobic nature of components which compose the system.

This background allows us to formulate a new mechanism of water absorption, which is viewed in the present article as a mechanism of micellar-entropy solvation of water, associated in clusters in micropores formed during absorption.

The fact that sorptional equilibrium of polymers with LMC is regulated by dispersion electromagnetic forces, which localize an admixture in the bulk of narrow micropores, gives an opportunity [8] to reconcile the well-known theory of vacancy solutions [13, 14] and theory of bulk filling of micropores (TBFM) [10].

According to the above model [8], absorption potential of the chain sponge can be presented as a function of the volume of absorbed molecules,

$$W = aV,$$

where W is the volume of formed equilibrium micropores; a is the absorption value; V is the molar absorbate volume.

Absorption potential, *i.e.*, the work of transfer of 1 mole of sorbed LMC into the equilibrium vapour phase

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

characterizes the work against sorption forces (here P and P_s are equilibrium pressures of unsaturated and saturated vapour of LMC,

respectively). Thus osmotic pressure on the sponge equals to

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

where $\Phi = \int_0^a ad\mu$ is the Gibbs integral due to Bangam [13], which characterizes a change of the chemical potential of the sorbent; $d\mu$ is the change of the chemical potential of sorbed substance. Definite values of a and P/P_s , which allows us to obtain the $A(W)$ dependency, correspond to each point of the sorption isotherm $W = aV$.

As a consequence of independence of dispersion forces on temperature, the function $A(W)$ is also independent on temperature. In this case, TBFM equation must be fulfilled [10]:

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

where E is the characteristic sorption energy; n is a constant.

For rigid-carass sorbents (of active coal type) $n > 2$ is usual and the value of E is high (10–30 kJ/mol). For polymers $n < 1$ and the value of E is low (0.5–3 kJ/mol) [15].

According to the TBFM, knowing of the isotherm for one temperature, an isotherm for another temperature can be calculated using more general equation [15]:

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

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

Applicability of Eqs. (1) and (2) in the equilibrium sorption of water has been demonstrated before for fibers of viscose, cotton, caprone, PVC, [15]. In this case, however, the sorption mechanism, defined by properties of the flexible-chain sponge, was not disclosed. In accord with the work [8], this process represents synthesis of a microporous sorbent directly under conditions of osmosis and is successfully described by the TBFM equation for both water and vapour of

oleophilic organic compounds. Applied to water, the TBFM equation gives an opportunity to clarify the question about its physical state in the polymeric matrix.

Analysis of Isotherms

Sorptional isotherms were calculated by Eqs. (1) and (2), coefficients of which were determined by the methods presented in [15,16]. Calculations indicated a complete accord of the TBFM equation with experimental points of isotherms for all polymers mentioned below. Figure 1 displays isotherms of hydrophobic polymers (25°C), given as typical examples in the book [2]. Corresponding values of coefficients in Eq. (1) for HDPE equal to: $a_0 = 3 \times 10^{-5} \text{ g/cm}^3$, $E = 2476 \text{ J/mol}$, $n = 1$.

Isotherms of the rest of polymers in Figure 1 are characterized by coefficients, which are listed below in the same order: 4.8×10^{-5} , 1500, 0.7 (LDPE, Fig. 1, curve 2); 5.6×10^{-3} , 780, 0.6 (fluoropolymer F-32, Fig. 1, curve 3); 10.4×10^{-3} , 1100, 0.7 (ethylene copolymer with vinyl-acetate).

Four isotherms of the sorption of water by synthetic polyisoprene Cariflex ($T = 36.6, 42.2, 50.3, 61.3^\circ\text{C}$, basic curve with $T_0 = 36.6^\circ\text{C}$ is shown in Fig. 2, curve 1) reported in the work [4] are described by Eq. (2) applying coefficients $a_{00} = 1.6 \text{ cm}^3 \text{ (STP)/cm}^3$, $E = 700 \text{ J/mol}$, $n = 0.55$, $\alpha = -0.02 \text{ grad}^{-1}$. Other isotherms in Figure 2 characterize the sorption of water at 50°C by synthetic polyisoprene Natsyn ($a_0 = 3.0 \text{ cm}^3 \text{ (STP)/cm}^3$, $E = 700 \text{ J/mol}$, $n = 0.55$; Fig. 2, curve 2), NR ($a_0 = 4.0 \text{ cm}^3 \text{ (STP)/cm}^3$, $E = 700 \text{ J/mol}$, $n = 0.55$; Fig. 2, curve 3) and weakly oxidized NR ($a_0 = 0.5 \text{ cm}^3 \text{ (STP)/cm}^3$, $E = 700 \text{ J/mol}$, $n = 0.55$; Fig. 2, curve 4).

Thus, calculations show that the sorption of water by all rubbers from the work [4] is defined by solvation entropy in the whole range of the relative vapour pressure. Formation of some amount of oxidized groups in NR increases absorption with no mechanism change.

As mentioned above, isotherms depicted in Figure 3 were used to distinguish the mechanisms of the water sorption by hydrophilic and moderately hydrophilic polymers. However, calculations indicate that the whole series of curves in Figure 3 responds to general mechanism of entropy solvation of water and are described by Eq. (1) under

following values of coefficients a_0 (g/g), E (J/mol), n :

- (1) Collagen ($a_0 = 0.65$ g/g, $E = 1200$ J/mol, $n = 0.6$);
- (2) PVC ($a_0 = 0.35$ g/g, $E = 900$ J/mol, $n = 0.7$);
- (3) Keratin ($a_0 = 0.27$ g/g, $E = 1500$ J/mol, $n = 0.6$);
- (4) CA ($a_0 = 0.15$ g/g, $E = 1200$ J/mol, $n = 0.7$);
- (5) Nylon-6,6 ($a_0 = 0.08$ g/g, $E = 1500$ J/mol, $n = 0.75$).

In a similar manner, isotherms from Figure 4 indicate the retention of the mechanism of entropy solvation during thermal modification of water soluble MAN-Vac copolymer. In this case, coefficients from Eq. (1) are changed as follows:

- (1) $C_{w0} = a_0 = 0.95$ g/g, $E = 1700$ J/mol, $n = 0.6$;
- (2) $C_{w0} = a_0 = 0.75$ g/g, $E = 1260$ J/mol, $n = 0.5$;
- (3) $C_{w0} = a_0 = 0.35$ g/g, $E = 1570$ J/mol, $n = 0.4$;
- (4) $C_{w0} = a_0 = 0.15$ g/g, $E = 1700$ J/mol, $n = 0.4$;
- (5) $C_{w0} = a_0 = 0.07$ g/g, $E = 1700$ J/mol, $n = 0.4$.

As seen, the copolymer transforming into a moderately hydrophilic state *via* the hydrogel stage does not reach the state of the rigid-carbass adsorbent.

It was shown that the isotherm of water sorption by lysocime, considered in the work [2], responds to Eq. (1) with coefficients $E = 640$ J/mol and $n = 0.4$, which differ just a little from the same coefficients (700 and 0.45, respectively) of the isotherm of *n*-hexane absorption by cellulose triacetate (CTA) films [8]. Thus, both cases display similar pseudo-Langmuir parts.

Taking into account the importance of the conclusion that the amount and quality of polar functional groups do not eliminate the mechanism of entropy solvation, we have also carried out calculations for other well-known hydrophilic polymers. For example, the water sorption isotherm by photographic gelatin of A trade mark (25°C) [17] is described by Eq. (1) with coefficients $a_0 = 0.6$ g/g, $E = 950$ J/mol, $n = 0.5$. The same coefficients for water in cellulose (25°C) [18] equal to 0.29, 2000, 0.7, respectively. For alginic acid (which main difference from cellulose is in the presence of a COOH-group instead of CH₂-OH), studied in the work [19] (30°C), these coefficients are 0.428, 1200 and 0.6, respectively. Salts (sodium and cobalt) of alginic acid

possess higher hydrophilic nature [19]. Coefficients of Eq. (1) for them are also similar (0.547, 1500, 0.6, respectively) in the range of $P/P_s < 0.9$, although sodium salt is dissolved in liquid water, and cobalt salt remains as a hydrogel and does not dissolve due to linking of polymeric chains by cobalt ions.

Thus, high hydrophilicity of a molecular-chain sponge possessing functional peptide, hydroxylic and carboxylic groups is combined with non-enthalpic mechanism of solvation of so-called "linked" water and displays energy interaction of the "water-water" type already in the range of lowest absorption values. It should be noted that formation of drops of free water is observed in the same polymers under quite high humidity [17, 19–21], but this does not affect coefficients of the TBFM equation.

Similar situation is observed in swollen ion-exchanging resins (anionites), the isotherms of which were calculated by us using the data of the work [22]. Corresponding graphics are displayed in Figure 5 as dependencies of the swelling degree, $V_s - V_d/V_d$, on P/P_s (here V_d and V_s are volumes of dry and swollen resin, respectively). As seen, swelling degree and curvature of the pseudo-Langmuir part in isotherms depend on the resin type. However, all isotherms in Figure 5 (curves 1–5) are described by Eq. (1). Their coefficients form the following numerical sequences:

- (1) $a_0 = 0.8 \text{ cm}^3/\text{cm}^3$, $E = 3900 \text{ J/mol}$, $n = 0.5$;
- (2) $a_0 = 0.55 \text{ cm}^3/\text{cm}^3$, $E = 2600 \text{ J/mol}$, $n = 0.9$;
- (3) $a_0 = 0.48 \text{ cm}^3/\text{cm}^3$, $E = 2300 \text{ J/mol}$, $n = 0.6$;
- (4) $a_0 = 0.31 \text{ cm}^3/\text{cm}^3$, $E = 2300 \text{ J/mol}$, $n = 0.6$;
- (5) $a_0 = 0.12 \text{ cm}^3/\text{cm}^3$, $E = 2600 \text{ J/mol}$, $n = 0.7$.

Of interest in the fact that isotherm of the equilibrium swelling of anionite AB-171 (Fig. 5, curve 2) can be considered as a straight line in the range of scattering of experimental points. Similar case is observed for HDPE (Fig. 1, curve 1), and this coincidence itself gives an opportunity to suggest an affinity of the water absorption mechanisms by a network polyelectrolyte to a hydrophobic polymer.

Concerning moderately hydrophilic polymers, whose chain units usually contain ester, amide and other polar groups, they do not introduce anything new into understanding of the isotherms. Thus,

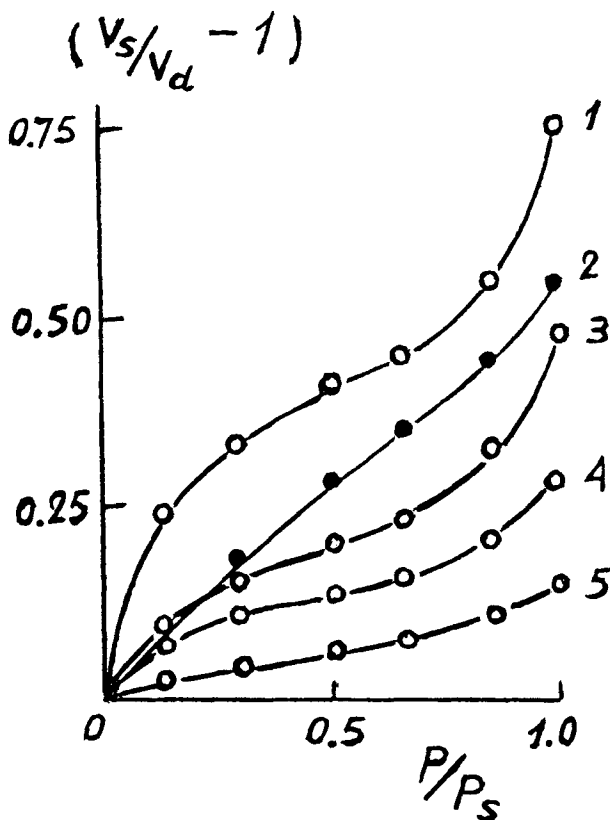


FIGURE 5 Swelling degree of anionites *versus* relative pressure of water vapour [22]. Resins: AB-178 (1), AB-171 (2), AH-221 D (3), AH-22 (4), AH-221-12/100 (5).

isotherms (30, 45°C) obtained for acetic PMMA (similar in properties to hydrophobic substances) in the work [23] display an *S*-like form and are described by Eq. (2) with coefficients: $T_0 = 30^\circ\text{C}$, $a_{00} = 0.024 \text{ g/g}$, $E = 1755 \text{ J/mol}$, $n = 0.7$, $\alpha = 6.3 \times 10^{-3} \text{ grad}^{-1}$. Their curvature is a little lower than that of a-PMMA samples from the work [24] (30°C), which possess coefficients $a_{00} = 0.023 \text{ g/g}$, $E = 1300 \text{ J/mol}$, $n = 0.7$. Isotactic PMMA films [24] (possessing coefficients $a_{00} = 0.06 \text{ g/g}$, $E = 750 \text{ J/mol}$, $n = 0.6$) differ from a-PMMA by higher expressed *S*-like form and increased absorption, although it contains 76% of the crystalline phase.

S-like isotherms are also displayed by more hydrophilic polymers from the sequence of moderately hydrophilic ones: Nylon-6 [5] (coefficients of Eq. (2) are: $T_0 = 5^\circ\text{C}$, $a_{00} = 0.135\text{ g/g}$, $E = 1850\text{ J/mol}$, $n = 0.7$, $\alpha = 0.002\text{ grad}^{-1}$), CTA [18] ($T = 25^\circ\text{C}$, coefficients are $a_0 = 0.13\text{ g/g}$, $E = 1250\text{ J/mol}$, $n = 0.7$), Nylon-6,6 [25] ($T = 25^\circ\text{C}$, $a_0 = 6.8\%$, $E = 1600$, $n = 0.7$), cyanoethylated cellulose with the substitution degree $\gamma = 287.3$ [26] ($a_0 = 8\%$, $E = 1250$, $n = 0.7$). Even the isotherm of ethylcellulose shown in the work [27], which displays poorly expressed pseudo-Langmuir part, is well described by Eq. (1) with coefficients $a_0 = 7.4\%$, $E = 800$, $n = 0.6$.

Clusterization of Absorbed Water

Results of this analysis allows us to conclude that water is absorbed polymers by "sorbate-polymer" interaction which, from the thermodynamic point of view, responds to the entropy of solvation whose energetics is stipulated by the primary "sorbate-sorbate" interaction. The absorption requires a structural work of reorganizing the initial sponge into the state of a microporous adsorbent. This work is provided by the osmotic pressure of sorbate vapour and the change of elastic tension of chains. Despite the reguluation of a part of sponge chain units by micropores, the overall change involves a definite increase of the configuration entropy of the system. The fact that the TBFM equation is valid for both water and oleophilic compounds indicates the repulsion of water molecules into the volume of micropores by short-range dispersion electromagnetic forces [10, 15, 16]. Thus, the thermodynamically equilibrium state of water in polymers is realized without any significant contribution of energetic interactions of water with polar groups of macromolecules.

Another important conclusion is related to the fact that the TBFM equation is valid in the entire range of the relative pressure of water vapour. This means that even at the lowest levels of filling, the equilibrium micropores do not include separate water molecules, but clusters of several associated molecules.

The observed wide distribution absorption values of polymers, is bound due to particular conditions of the hydrophilic-hydrophobic force balance, involving the counteraction of two main factors. One is

the already mentioned stabilizing factor, connected to an increment of the configuration entropy associated with the formation of a fringed layer around the micelle nucleus. The other is a destabilizing effect of hydrophobic push of water by dispersion forces from capsule walls into the volume of the equilibrium micropore.

From general ideas it is evident that the hydrophobic force in a micropore depends on the structure of its units and curvature of its surface. Existence of polar groups (carriers of constant electric charges) in the capsule must reduce the contribution of dispersion (that is fluctuational) electromagnetic forces. This reduces the repulsive forces of the water and, consequently, the size of micropore must increase. Simultaneous decrease of the surface curvature will reduce compression of cluster by its surface tension increasing the number of water molecules in the cluster.

The clusters encapsulated in micropores are able to decrease their surface energy by coalescence. Coalescence of clusters does not change their total volume, but decreases both their total surface and the surface energy. Simultaneous release of units from the structure of capsules and reduction of the total elastic load of chains must increase the configuration entropy of the system and promote growth of the absorption.

At low levels of filling, of the sponge by water, the difference between hydrophobic and hydrophilic polymers at low filling degrees are relatively small, because the primary clusters possess small total volume and reduce the total tension of the sponge. A more or less polar polymer is wetted and the number of primary clusters inside cells of paracrystalline (or crystallite) carcass increases and the stage of reduction of the elastic loading on the sponge is stopped. With increased wetting, the growth of the number of clusters begins impeding the absorption because of the increase of the elastic loading of the sponge. This is expressed in the appearance of a more or less clear saturation part on the isotherm, characterized by the sorption on a limited number of active centers under the Langmuir mechanism.

In the general case, many factors are meaningful for the configuration entropy of the sponge (size, structure and methods of chain units linking, degree of substituents distribution along the macromolecule, initial degree of highly elastic tension of the sponge). For example, turning back to the above mentioned example of increased absorption

of *i*-PMMA in comparison of that of *a*-PMMA, it can be expected that the sponge of *i*-PMMA would possess a higher potential of the entropy increase. Non-crystalline phase of *i*-PMMA, indeed, indicates low glass transition temperature $T_g = 50^\circ\text{C}$ ($105\text{--}115^\circ\text{C}$ for *a*-PMMA) [28] and increased highly elastic volume tension of chains, stipulated by transversing certain sponge chain links into crystallites. This combination of properties of *i*-PMMA reduces the pressure on water clusters from the hydrophobic walls of entropically stabilized capsules-micropores. Thus, the clusters obtain an opportunity to increase their size.

Of important role for the sponge entropy is also the chain rigidity. Introduction of rigid segments into chains decreases the number of conformations performed by the sponge. Thus, the increments of the configuration entropy must also decrease. Such situation takes place for segmented polyetherurethane, the chains, of which consist of flexible (polyester) and rigid (polyurethane) segments [2]. The calculation shows that corresponding isotherms (25°C) depicted in [2] are described by Eq. (1), coefficients of which for a polymer with 28% of rigid segments equal to $a_0 = 1.8\%$, $E = 1180\text{ J/mol}$, $n = 0.8$, respectively. For a polymer with 44% of rigid segments these indexes are $a_0 = 0.9\%$, $E = 950\text{ J/mol}$, $n = 0.9$. As seen, increase of rigidity is significantly reflected in water absorption without changing the mechanism of solvation of its clusters.

From the above-mentioned it follows that thermodynamic function of polar groups of macromolecules is to affect the configuration entropy of the system and intensity of the hydrophobic localization of water clusters in volumes of micropores and not to form local bonds with water molecules.

Enlarging of clusters with increase of the sponge humidity decreases curvature of micropores until the pores assume the chinks with plane walls. On this stage the maximum difference between hydrophobic and hydrophilic polymers is displayed. A new thermodynamic factor, the wedging pressure, is connected to chink micelles. It is discussed in detail in the book [29]. In chinks with hydrophilic walls, it is positive and stabilizes the water interlayers. The important factor in this stabilization is the structure of adsorbed layers, imposed to water by active surface centers. The formation of stable water interlayers is observed, for example, with hydrophilic polymers during thermo-mechanical and dielectric measurements [19].

Contrary to hydrophilic chinks, the water interlayers in hydrophobic chinks are affected by negative wedging pressure. Water molecules in these chinks exist under stronger mutual interaction. This in turn reduces the water density on the chink walls interface [29].

The presence of the cluster structure in water under any humidity of the sponge must be taken into account in simulations of water properties in polymers. For this purpose, of special interest are experimental data [30] on IR-spectra of water in CA in CTA films. The authors of this work [30], attribute great importance to local energetic bonds with ester groups. Nevertheless, the analysis of presented dependencies of optical density (D) of the main bands of IR-absorption of water on the value of P/P_s (25°C) indicates their compliance with Eq. (1). For CA equilibrium dependency $D(P/P_s)$ is characterized by coefficients $E = 900\text{ J/mol}$ and $n = 0.5$ similarly for bands of 3600 , 3400 and 1610 cm^{-1} for values of D_0 of 0.33 , 0.45 and 0.15 , respectively. Thus, three mentioned isotherms can be transformed into each other, which indicates the general mechanism of changing of mentioned bands of water absorption during entropy solvation.

In the case of CTA similar dependency is described by Eq. (1) with coefficients $E = 1250\text{ J/mol}$ and $n = 0.7$ for absorption bands of 3630 , 3550 and 1640 cm^{-1} at corresponding values of D_0 equal to 0.45 , 0.4 and 0.3 respectively. Present curves also transform into each other and, moreover, can be transformed onto the water sorption isotherm by CTA films, given in the work [18] and described by Eq. (1) with the same coefficients E and n at $a_0 = 0.13\text{ g/g}$. Moreover, all mentioned isotherms are transformed onto the isotherm of water sorption by cyanoethylated cellulose films with the substitution degree $\gamma = 287.3$, studied in the work [26] (it coefficients were $a_0 = 8\%$, $E = 1250\text{ J/mol}$, $n = 0.7$).

The reported transformation of equilibrium sorptional curves shows that substitution of acetate groups by more hydrophobic cyanoethyl ones does not change the general mechanism of entropic water linking. The observed decrease of the water absorption is therefore, not provided by substitution of local energetic bonds, but by the change of the above described force hydrophilic–hydrophobic balance in the structured sponge.

Structural Effects Conjugated with Water Absorption

Thermodynamic entropy type of the water-polymer interaction does not exclude energetic interactions of the water-polymer type. These interactions are realized, for example, in processes of functioning of ion exchange resins. As shown before, the swelling of polyelectrolytes is ruled by the mechanism of entropic solvation, but the very fact of the ion exchange tensifies the presence of local contacts between capillary water and active centers of macromolecules. It is natural that a definite probability of such dynamic interactions must also exist for water clusters a low filling levels of the sponge. However, the energetic contribution of these processes is not the deterministic measure for the general thermodynamic type of the equilibrium absorption.

Predominant value of the structural-entropic way of water absorption is connected to the structural reorganization of the initial molecular-chain sponge. This implies the occurrence of a number of interesting events, that cannot be explained independently of energetic interactions.

This particularly relates to the well-known effect of sorption-desorption hysteresis. If reconstruction of the sponge induced by absorption causes the formation of chink micropores with walls possessing quite high hydrophilicity and strength, then isotherm of the equilibrium desorption of LMC can differ from the absorption isotherm. In this case, the observed hysteresis loop is most clearly displayed by polymers with relatively rigid chains (by cellulose, for example [20]).

The picture of this hysteresis can be described in the following manner. During water absorption, swelling spongy granules of hydrophilic and quite rigid-chain polymer accumulate large amount of water in chinks that open during water absorption and are absent in the dry polymer. During water evaporation from these chinks, menisci with negative curvature are formed in the chinks. As known [10], these menisci with negative curvature differ from the plane surface by reduced equilibrium vapor pressure. In accordance, with the geometry of spongy granules, many of chink micropores are radially oriented. Therefore, their walls are drawn together in direction to the center of granules. Meniscus curvature in them increases with water evapora-

tion, which requires additional reduction of the equilibrium pressure of vapour. Consequently, isotherms of the equilibrium desorption indicates a rather extended histeresis loop.

Occurrence of capillary phenomena also accompanies water absorption in hydrophobic polymers. These phenomena are characterized by their fluctuational nature and are most clearly displayed at temperature above T_g transforming the equilibrium absorption into the kinetic process of spontaneous separation of droplets of water in the polymeric matrix [9].

Phase-excretion of water is provided by fluctuational pulses of chink micropores, during which their hydrophobic walls undergo isothermal fluctuations. During the fluctuational compression of chinks, the water interlayers are pressed out forming growing drops of liquid water. During growing, the drops compress highly elastic matrix decelerating the action of the "fluctuational pump" and shifting the absorption into the regime of pseudo-normal sorption. Under this regime, the rate of water absorption by the sponge of devitrified polymer is limited by viscous flow of macromolecules in the field of mechanical forces of growing conglomerate of water drops. This process is accompanied by significant deformation of sample [9].

If the sorption temperature is higher than the boiling point of water, the drops of water are not formed in a polymeric matrix. However, the cooling of devitrified polymer impregnated by water causes formation of very small drops of water in the matrix. They deform the matrix and change many of its physical properties. The mentioned effect was observed for PE, polycarbonate, polysulfone [31], polystyrene and polyepoxide [32].

Let us mention one more interesting fact which expresses entropic-solvation effect of sponge and is connected with the features of radiation modification of cellulose. It was reported [33] that swelling of cellulose in hydrophobic solution of styrene in the absence of water is in sufficient for radiation grafting of styrene to macromolecules in the bulk of the samples and is limited just to grafting on the surface. Nevertheless, the presence of 2% of water in the system significantly increases absorption of styrene and its accessibility to active centers. Consequently, radiation grafting in the bulk of samples proceeds with high efficiency.

It is evident that the mentioned effect cannot be explained by formation of hydrogen bonds between water and cellulose. These

bonds cannot impart the hydrophobic property to cellulose required for swelling in a hydrophobic liquid. However, pith of the effect can be easily understood, if we take into account that the main state of water in cellulose is presented by entropic-solvation clusters. On entering the molecular-chain sponge of cellulose, the separate molecules of water are clustered. By realizing the exothermic effect of clusterization, the clusters extend chain units and form from them capsules of dynamic fluctuating micropores. Since the clusters are the element of the spongy structure undergoing periodical fluctuations, they decompose and aggregate back again, transporting water in the volume of the spongy matrix. Under conditions of rather high vapour pressure, styrene contains pores which become free from water and which styrene cannot form by itself because of insufficient energy of the "sorbate – sorbate" type.

Heat Effects Conjugated with Water Absorption

The concept of entropic-solvation mechanism of water absorption by polymers, discussed in the present paper, is based on the formation of a microporous structure under conditions of absorption. The characteristics of this formation is demonstrated with the help of the well-known TBFM equation for microporous adsorbents. This equation gives us the opportunity to disclose the physical sense of observed difference between the signs of apparent enthalpies of "sorption", ΔH_s , and "dilution", ΔH_a . It is known that the application of Henry's law to initial parts of sorption isotherms usually gives negative values of ΔH_s , both in the case of polar polymers [2, 3] and at negligibly small content of polar groups, existing in rubbers, PE, PP [4, 34]. The value of ΔH_a , calculated in this case, is usually positive, which does not follow the usual trends of these enthalpies [10].

Looking at Eq. (2), it can be easily observed that in the Henry law substitutes by the indexes, RT/E and n are substituted by unity, which leads to

$$a = a_{00} \left(\frac{P}{P_s} \right) \exp[-\alpha(T - T_0)] = K_g P,$$

where $K_g = (a_{00}/P_s) \exp[-\alpha(T - T_0)]$.

Taking into account [35] that

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

where λ is the heat of water evaporation, B is the constant, we obtain the expression for the constant

$$K_g = \left(\frac{a_{00}}{B}\right) \exp\left[\frac{\lambda}{RT} - \alpha(T - T_0)\right].$$

The value of K_g for the above mentioned polymers decreases with increasing temperature. This shows that the exp-multiplicand index is positive. Therefore, the calculations made in accordance with the Henry law and performed on the basis of usual temperature dependency

$$K_h = \text{Const} \cdot \exp\left(\frac{-\Delta H_s}{RT}\right),$$

give a negative change of enthalpy. In this connection, a concept has been formed in the literature that the positive heat effect is produced due to energy interaction of the water-polymer or water-hydrophilous admixture.

Nevertheless, the above shown transformation of Eq. (2) shows that the effect is connected to the work of water transfer from sponge into vapour phase upon equilibrium condition, *i.e.*, it is stipulated by endothermic desorption of water from clusters, already formed in the sponge under the lowest filling degree. When such work is realized under the condition $\alpha = 0$, the calculated value of ΔH_s corresponds to the evaporation heat of normal water, λ . In the general case, coefficient α can have a negative or positive value. Thus, the heat effect of absorbed water evaporation can either exceed or be lower than the condensation heat of usual water.

Under conditions of $a = \text{Const}$ and $n = 1$. Eq. (2) is transformed into

$$\frac{P}{P_s} = \exp\left\{\left[\ln\left(\frac{a}{a_{00}}\right) + \alpha(T - T_0)\right] \cdot \frac{E}{RT}\right\}.$$

Here, the ratios $a/a_{00} < 1$ and $\alpha \ll 1$ provide negative index of the exponential multiplicand on the entire interval of P/P_s values (if $\alpha < 0$) or on a significant part of this interval (if $\alpha > 0$ in consequence of $\alpha \ll 1$ and small value of $(T - T_0)$). In the present case, applying usual dependency

$$\frac{P}{P_s} = \text{Const} \cdot \exp\left(-\frac{\Delta H_a}{RT}\right),$$

we will obtain positive value of ΔH_a . In accordance with this transformation of Eq. (2), endothermic features of "dilution" is high at low degree of sponge filling by water and decreases with its growth.

Thus, the TBFM equation discloses the facts that the energetic interaction in the polymer sponge is due to the "water-water" type. The formation of equilibrium water clusters proceeds already at lowest levels of filling, and more or less strong pressure on clusters from the side of the molecular-chain sponge transformed into a microporous structure.

CONCLUSION

The performed analysis confirmed the absence of free exchange of locales between LMC molecules and chain units in the polymeric matrix. This limits the range of applicability of homogeneous-statistical approaches to rather diluted solutions of polymers. The systems involving a molecular-chain sponge require now a approach to treat the physical chemistry phenomena of the system.

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