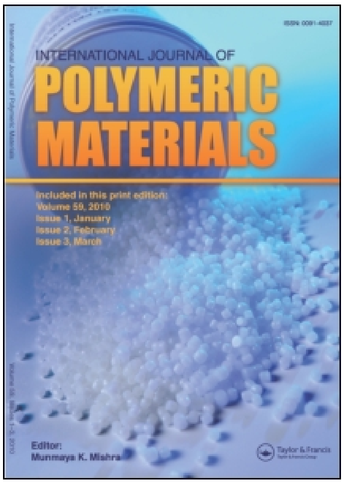

International Journal of Polymeric Materials

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

The General Aspects of Diffusion of Water in Polymers

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To cite this Article Iordanskii, A. L. and Zaikov, G. E.(1994) 'The General Aspects of Diffusion of Water in Polymers', International Journal of Polymeric Materials, 24: 1, 193 — 209

To link to this Article: DOI: 10.1080/00914039408028565

URL: http://dx.doi.org/10.1080/00914039408028565

Intern. J. Polymeric Mater., 1994, Vol. 24, pp. 193–209
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Printed in Malaysia

The General Aspects of Diffusion of Water in Polymers

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The general affects of diffusion of water in polymers are reviewed and discussed.

KEY WORDS Diffusion, water, polymers

RESULTS AND DISCUSSION

The unique structure of water and its huge deposits, ready availability and attractive technological properties make it the most common solvent for chemical and biochemical substances.

The intensity of the interaction of a polymer matrix with water molecules and species of chemically and biologically active media depends considerably on the polarizability and polarizing capability of the macromolecular fragments. It defines considerably (if not on the whole) the mechanism of diffusion transport in polymers.

At present, all the known polymers are defined by their difference in water content. Of course, it is a great oversimplification of the main characteristics of the polymers and their water interactions, but nevertheless it is a convenient approximation for practical purposes. A question should be advanced before we turn to discussing the problem of diffusion of water in polymers. "Are there any specific features in water sorption-diffusion mechanisms in hydrophobic and hydrophilic polymers?"

A successful attempt to classify polymers according to their hydrophilicity was made with the help of the solubility parameter δ characterizing the intensity of intermolecular interactions or cohesion energy.[1]

According to the Flory-Huggins theory water dissolubility in a polymer is connected to the solubility parameters:

$$\ln \varphi_w + \varphi_p + \chi\varphi_p^2 = 0, \qquad (1)$$

where

$$\chi = \chi_H = \bar{V}_w(\delta_w - \delta_p^2)/RT. \qquad (2)$$

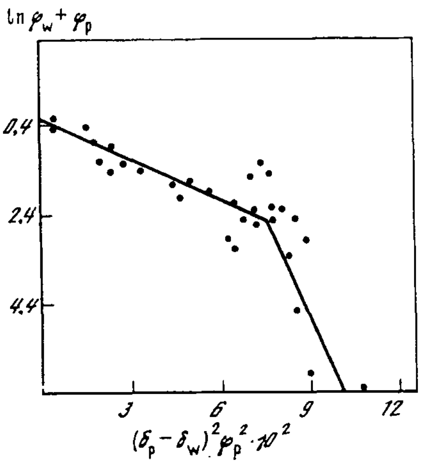


FIGURE 1 Solubility of water in polymers in accordance with Flory-Higgins equation.

Here χ is the nondimensional Flory-Huggins parameter, its enthalpic part; φ_i is the volume quotas of water (w) and polymer (p) in the system.

From Equation (1) it is seen that ($\ln \varphi_w + \varphi_p$), which depends on the square of the difference in solubility parameters multiplied by φ_p^2, is linear. However, the analysis of the solubility of 45 polymers of different hydrophilicity shows that the dependence is nonlinear and may be approximated by two divisions, where the value of the product $(\delta_w - \delta_p)^2\varphi_p^2$ is <600 J/cm³ for one type of hydrophilic polymer and >800 J/cm³ for the other.[2]

The values correspond to the point of intersection of the division that characterizes the moderately hydrophobic polymers (Figure 1). The transition from hydrophobic polymer to hydrophilic polymer reflects the appearance of an entropy noncombinatorial term of the Flory-Huggins parameter, which upsets the additive nature of the polymer-water system's total volume change. That is a characteristic of hydrophilic polymers, whose functional groups interact actively with water.

WATER SORPTION IN HYDROPHOBIC POLYMERS

According to the above mentioned classification, polymers containing less than 0.5–1 weight percent of water under normal conditions (Reference 3, p. 41) should be classified as hydrophobic. Polyolefins, fluoroplasts, rubbers, polysiloxanes, and a number of simple and complex polyesters, nonplasticized PVC and some others are of this type. Thus the majority of high-tonnage polymers widely used in various branches of industry, especially as corrosion-stable construction materials and covers should be classified as hydrophobic polymers.

That is why such structure sensitive parameters, as solubility, permeability and water diffusion coefficients, can significantly differ for a given polymer depending on the method of production and the sample's history. In other words, it depends upon the degree of damage to the polymer's chemical structure. This fact unconditionally impedes the creation of a numerical theory for water diffusion in polymers.

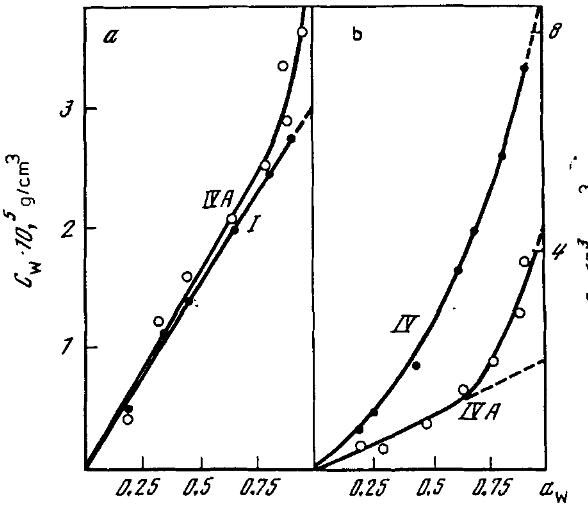


FIGURE 2 Typical sorption isotherms for hydrophobic polymers; (a) PEHD (I), PELD (IYA%); (b) copolymer ethylene with vinylacetate (IY%), fluoropolymer F-32 (IYA%).

The water sorption isotherm for hydrophobic polymers under normal and slightly increased temperatures either conforms to Henry's equation, or shows a positive deflection from linearity (see Figure 2).

To interprete the nonlinear character of the sorption isotherm several models are used. The most popular of them are: 1) model of multilayer adsorption or BED; ii) theory of polymer solutions by Flory; and iii) cluster formation model by Zimm-Lundberg.

It is important to differentiate cluster formation in binary diffusion systems of polymer-water from water association, occurring around hydrophobic impurities and inculcation groups. In water associates, formed by the hydration of ionogenic and polar groups, as shown by NMR and IR data, free molecule immobilization is significantly higher than that for pure water clusters, stabilized by hydrogen bonds. It is practically impossible to create an unalloyed "pure" polymer. That is why a real polymer can contain: i) homogenous dissoluble water, existing as separate molecules; ii) water clusters; iii) hydrated water of polymer functional groups (inculcation groups); and iv) water, immobilized on polymer impurities. As α_w changes, one of these mechanisms may prevail over the others, simplifying the numerical consideration of diffusion and sorption.

The process of water cluster formation may be presented by a number of consecutive reactions:

$$\begin{array}{ll} w + w = w_1 & (K_1), \\ w + w_1 = w_2 & (K_2), \\ \cdots\cdots\cdots & \cdots\cdot, \\ w + w_{n-1} = w_n & (K_n), \end{array} \tag{A}$$

where w is the symbol of a free water molecule; $w_1, w_2, \ldots, w_n$ are symbols of water clusters with same number of molecules $2, 3, \ldots, n+1$; the corresponding equilibrium constants are shown in brackets.

The total water concentration in the polymer, as shown in reaction Equation (A), is:

$$C_w = C_{wf}\left[1 + \sum (i+1)\left(\prod K_i\right) C^i_{wf}\right], \tag{3}$$

where C_w and C_{wf} are concentrations of free and total water in the polymer; $\Pi\ K_i$ is the multiplication of i constants.

When adsorption centers (hydrophilic groups) are slightly filled with water the Langmuir isotherm shows linear character, and the model of dual sorption[4] is also a linear equation

$$C_w = (K_H + S_{pf}K_L)\alpha_w = K_H\alpha_w, \tag{4}$$

where S_{pf} are the concentrations of inculcation groups; K_L is the Langmuir effective constant; $K_H = K'_H + S_{pf}K_L$.

Actually, the treatment of experimental results for water sorption in a typical hydrophobic polymer (PELD Medical Grade F CSFR, fluoroplast-2M, fluoroplast-32) has shown, that among all the water associates the portion that is N-mers of

TABLE I

Diffusion parameters in polymer-water systems

Polymer	$C_w 10^3$, g/g	$K_H 10^3$, g/g	$K_{HT} 10^2$	N_c	ΔH, kcal/ /mole	$D_{wf} 10^3$, sm^2/s	$D_N 10^9$, sm^2/s	Notes
PEVP	0,036	0,036	-	1,0	5,9	2,3	-	A
PELD	0,051	0,041	1,0	1,4	6,2	2,6	>0,5	B
F-10	0,80	0,80	-	1,0	8,5	1,5	-	C
F-2M	2,1	0,70	0,16	2,5	5,7	3,4	2,2	C
F-32	4,4	1,2	0,54	2,5	8,5	1,3	2,5	C
PEVA	10,5	2,6	0,34	1,7	-	1,4	0,92	D
PEVA	16,0	4,1	0,12	1,7	-	0,65	1,0	E
PVC	8,1	1,2	0,22	2,1	5,1	7,5	1,6	F

A is from literature data at 37°C; *B* is for a "Medical Grade" at 37°C; *C* is the water flow registered chromatographically at 50°C; *D* is ethylene and vinylacetate copolymer with a molar ratio of 6:1 at 37°C; *E* is the same for copolymer with a molar ratio 3:1; and *F* is for contained plasticizer residues of 3–5% dioctylphthalate at 37°C.

definite types (see Figure 2 and Table I (IVA type polymers)) is the largest. That is why Equation (4) is transformed into a more simple one describing a bimodal distribution of water clusters:

$$C_w = K_H(p/p_0) + N\left(\prod^{N} K_i\right)(K_H[p/p_0])^N, \tag{5}$$

where $N = n + 1$.

The graphical solution of Equation (5) in $\lg[C_w/C_{wf}) - 1] - \ln(p_0/p)$ permits determination of the effective constant of the sorption processes $G = \Pi K_i$ and the number of molecules N in a cluster (see Table I).

A model for the filling of the ligand centers (or sorption centers, by analogy) can be used as one of the physical assumptions.[5] The equilibrium constants of a consecutive reaction series (A) $K_1, K_2, \ldots, K_n$ can be expressed through an immobilization constant K_T:

$$K_i = K'_T(N - i)/i.$$

Under such an approach the existence of an adsorption center, reversibly filled by N adsorbant molecules is assumed. In our interpretation it may be N water molecules forming a water associate. Taking into account this assumption, we can show that Equation (4) transforms into

$$C_w = C_{wf}(1 - K'_T C_{wf})^N \left[\frac{1 + NK_T C_{wf}}{1 + K_T C_{wf}}\right]. \tag{6}$$

Let us note, that the multiplicand in square brackets defines the average clustering number $\hat{N}_c$. An analysis of Equation (6) shows, that under the condition $K'_T C_{wf} << 1$ and $NK'_T C_{wf} << 1$ cluster formation does not occur and Equation (6) transforms into the Henry equation, and for $K'_T C_{wf} >> 1$ becomes

$$C_w = (N + 1)(K'_T)^N \cdot C_{wf}^{N+1},$$

This reflects a sharp increase in the sorbed water content in the polymer. According to the above discussion, polymeric systems described by Equation (6) should be characterized by isotherms of the IV type. PVC and copolymers of vinylacetate with ethylene (PEVA) may serve as examples of such polymers (see Table I).

Analysis of the results for equilibrium water sorption by isothermal classification polymers of various types, presented in this table, show the correctness of the isothermal classification by types (I, IV and IVA). For polyolephins and tetrafluorethylene of high crystallinity (high density) clusters do not form at room temperature over the entire interval of α_w. Isotherms of that type (type I) are described by the Henry equation. For PELD (a polymer for medical applications) at high temperatures and large values of α_w a noticeable deflection from linearity (see

Figure 2) is seen due to water associate formation in the polymer. In this case isotherms of IVA type are described by Equation (5). Isotherms of an analogous type are characteristic of fluoroplasts F-32 and F-2M. Literature data on water sorption by polyoxymethylene and polydimethylsiloxane (PDMS) can also be analyzed within the suggested model. The coincidence of average clustering numbers calculated by us with the help of the Zimm-Lundberg equation and Equations (5) and (6), reveals the correctness of the cluster model, considered in this section. The third type of isotherm (type IV) is satisfactorily described by Equation (6). The parameters K_T and N_c are placed in the corresponding columns of Table I.

The change in the constant K_H relative of the Henry equation during transition from one polymer to another can also be seen in that table. Analysis of Equation (4) brings us to the same conclusion, if the concentration of centers (inculcation groups) in the polymer is regarded as dependent on its nature, prehistory, and degradation degree during production and use. It shows visually the role of various levels of imperfections of the sorption-diffusion process in polymers. Unfortunately, a great number of authors point out only the linear character of water sorption by hydophobic polymers, without analysis of the mechanism of this phenomenon.

At the same time, the calculation of average water clustering number showed that this number differs little for various polymers. This fact is understandable, as water-water interaction in a hydrophobic matrix prevails over that for water with the macromolecule. The benefit of the predominant of the interaction between sorbed water molecules is confirmed by the fact that the values of sorption heat ($-\Delta H_S$) for high activities are close to those of the heat of condensation for water and are nearly invariable for the majority of polymers presented in Table I.

Thus, sorption behaviour of water molecules in hydrophobic polymers seems rather complex. For very low concentrations of water (10^{-5} mole/g) even for relatively low-impurity polymers it is necessary to take into account the immobilization of water molecules on hydrophobic centers ("inculcation groups"). In the field of high vapour pressures the possibility for cluster formation (heterogeneous fluctuations—after Frenkel) must be taken into account. The dependence on the concentration intervals of corresponding models and mathematical apparatus should be used.

WATER DIFFUSION IN HYDROPHOBIC POLYMERS

It is impossible to describe the process of diffusional transport with regard to cluster formation in the range of a "total immobilization" model. One must take into account the movement of water associates that contribute significantly to the total flux. That is why the forthcoming consideration is advisable to perform in the range of a "partial immobilization" model. For the case of free molecules, dimers, trimers, etc. (each fraction with its own diffusion coefficient) taking part in transport, the water flow in the polymer can be written as:

$$J_{wi} = -\sum^{N} iD_i \nabla C_{wi}, \tag{7}$$

where D_i are the partial diffusion coefficients of water associates with a molecular number equal to 1, 2, 3, . . . , N.

Equation (7) was written in accordance with the equation system (A) and by the suggestion that cross diffusion coefficients of water are close to zero. Further transformation of the equation, using designations, included earlier, leads to this expression for the total water flow:

$$J_w = -\sum_i^N iD_iG_i(K_H\nabla\alpha_w)^i. \tag{8}$$

With the help of a penetration definition

$$P_w = \sum_i^N D_iC_i,$$

we can transform it to the expression for an effective diffusion coefficient D_w.

The integral (effective) diffusion coefficient can be written in a generalized form:

$$D_w = P_w/C_w = \sum iD_iG_i(K_H\alpha_w)^i \Big/ \sum iG_i(K_H\alpha_w)^i, \tag{9}$$

where i is the number of molecules in a cluster with regard to monomolecular water; G_i is the product of the constants of cluster formation and the disintegration reaction is in accordance with the system of Equation (A).

If $i = 1$, Equation (9) describes the trivial case for the movement of single water molecules.

DIFFUSION IN FLUOROPLASTS: PARTIAL IMMOBILIZATION MODEL

Among the great number of fluoro-containing polymers, applied as anticorrosion protection for metal articles, fluoroplasts of F-4, F-40, F-4MB types, used as brick-lining materials, are the most widely used, and also F-10, F032, F-2M, which can be used as plate monoliths and laminated compositions. During contact with aggressive media, fluoroplasts can also be used as structural materials for the production of elements for mains, thermoexchange devices, rubbed parts for engines and pumps (F-4MB, F-2M).

Fluoroplasts with a lower percent of crystallinity (F-2M and F-32L) sorbed an appreciable quantity of water (0.08 and 0.03% correspondingly). At higher temperatures their water content increases sharply and reaches, respectively, 0.19% and 0.42% at 50°C, while for the three polymers F-4, F-4MB and F-40, mentioned previously, water sorption does not exceed 0.1% even at the temperature of boiling water.

$$J_w = -D_{wf}K_H\nabla\alpha_w - ND_NG_N(K_H\nabla\alpha_w)^N \tag{10}$$

where D_N is the N-mer diffusion coefficient and a number.

DIFFUSIONAL TRANSPORT, COMPLICATED BY CONTINUOUS DISTRIBUTION OF SIZES OF WATER ASSOCIATES

The suggestion to fill a certain hydrophobic center (cavity), able to sorb N water molecules in accordance with the ligand model of Tenford,[6] makes it possible to write down water penetration in the form of:

$$P_w = P_{wf}(1 + K_T\alpha_w)^N[(1 + NK_T\alpha_w)/(1 + K_T\alpha_w)], \tag{11}$$

where P_{wf} is the free water molecule penetration $P_{wf} = K_H\alpha_w D_{wf}$; Equation (11), in combination with the expression for concentration, permits us to generate an expression for the integral coefficient of water diffusion:

$$D_w = P_w/C_w = D_{wf}\left[\frac{1 + K_T\alpha_w}{(1 + K_{HT}\alpha_w)^{N-1}}\right]\left[\frac{1 + (N + 1)K_T\alpha_w}{1 + (N + 1)K_{HT}\alpha_w}\right]. \tag{12}$$

Ratios for the penetration and diffusion coefficients were obtained under the assumption that the partial diffusion coefficient of every associate, containing i molecules correspondingly, is determined by:

$$D_{wi} = D^0_{wf}\exp[-iV_w/BV_f],$$

i.e., grows exponentially due to the decrease in the number of molecules in associates. If $i = 1$, this equation defines the diffusion coefficient of free water:

$$D_{wf} = D^0_{wf}\exp[-4\pi R^3_w/BV_f\}. \tag{13}$$

Analysis of Equation (12) shows that it is transformed into a simple expression describing free water diffusion if $K_T\alpha_w << 1$ and $NK_T\alpha_w << 1$ in Equation (13). Equation (12) is also supplied if $K_{HT}\alpha_w >> 1$

$$D_w = D^0_{wf}\exp[-K_RN]. \tag{14}$$

i.e., for a high concentration of water transport it can be described by a diffusion coefficient decreasing exponentially due to the increase of the number of water molecules in the associate.

Stationary transport of water through films of statistical copolymers of ethylene and vinylacetate (85:15, 75:25, molar %) give experimental confirmation of the suggested model. Figure 3 represents the concentration dependence of penetration and the effective coefficients of water diffusion, calculated from the corresponding equations (curves) and experimentally determined. The decrease of $D_w(C_w)$, as in the previous cases, reflects the partial immobilization of water molecules in associates, the latter being mostly effective at the starting section of the isotherm. This case differs significantly from the previous situation, described for fluoroplasts.

Sorption isotherms, described well by a number of constants (K_H, K_{HT} and N) given in Table I, testify to the participation of N types of particles in the transport

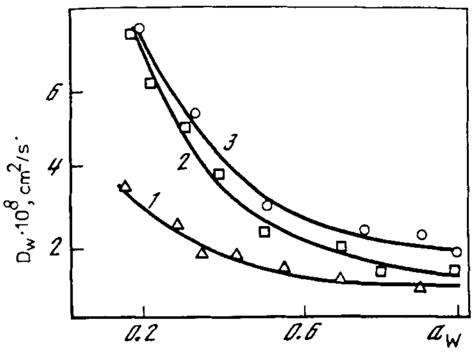


FIGURE 3 Water diffusion coefficient in copolymers of ethylene with vinylacetate 85:15 (1), 75'25 (2) and in PVC (3).

process. Each particle has its own partial coefficient. A good approximation of the experimental results confirms the association model under stationary conditions of diffusion transport through hydrophobic polymer covers, wrappers, and films. Let us also point out that the motion of free water molecules and associates of various structure with their own characteristic rates occurs as a principally new aspect of sorption theory development. It can be used to describe not only water diffusion, but other low molecular weight components also (solvents, stabilizers, etc.), which combine with the polymer (not necessarily hydrophobic) rather badly and are able to form a number of associates.

Thus, diffusion in hydrophobic polymers is characterized not only by a low concentration of dissolved water, but also by the possibility of partial immobilization on hydrophilic inculcation groups and by the formation of cluster structures. The concentration of impurity groups, created in the polymer by damage to oxidation of the primary macromolecule or by residues of catalysts, etc., depends on the history and the production process of the samples. That is why the measurement and calculation of diffusion coefficients must include information about the content and distribution of these groups throughout the thickness of the sample.

WATER SORPTION IN HYDROPHILIC POLYMERS

A polymer is called hydrophilic if it contains 10 volume percent (v.p.) of water at 25°C and 100% atmospheric humidity.[3] This 10% criterion is rather conventional as it does not determine the state of water in the polymer and cannot verify the diffusion transfer mechanism. The amount of water in the polymers depends on the nature of the hydrophilic groups, i.e., on their polarizability and polarization, as can be seen from Table 2.4 in Reference 7. Each functional group is characterized by a certain number of water molecules $H_w \cong 1$ decreasing as the content of nonpolar hydrocarbon increases (see PVA, soapy vinylacetate and ethylene copolymer). For hydrophilic polymers (polyalcohols, polyacids, proteins, cellulose, some polyamides, poly-α-vinylpyrrolidone, etc.) group input values are close to or exceed this value.

Moderately hydrophilic polymers have a value of about $(1-3)\cdot 10^{-1}$, whereas for hydrophobic polymers it is $H_w \leq 10^{-2}$.

Isotherms of water sorption by hydrophilic polymers differ greatly from those for hydrophobic polymers. The characteristic inflection point and *s*-form at low and moderate water concentrations (initial isotherm) appear because of the strong interaction of water molecules with highly polar polymer residues (Figure 4).

When the sample is at a temperature above or below the glass transition temperature the anomalous behaviour of the isotherms should be explained in different ways.

The entire concentration interval up to a relative humidity of $p/p_0 = 1$, where keratin absorbs 33% water, may be divided into three sections. In each of them the process of sorption proceeds as in a hydrophilic polymer-water system. First water interacts with the most polar or ionizable protein residues. Water becomes strongly bound and makes an initial hydration sphere. The hydration heat of this isotherm section is maximally ≅80 kJ/mol H_2O, and the partial mole volume of the water molecules is considerably more than for free water so that this section of the isotherm goes up sharp (Figure 4). When the relative vapour pressure becomes about 0.1 (5% of water in the polymer) the number and volume of water associates in the vicinity of the hydrophilic groups increases. As the humidity increases, less polar groups become hydrated. The sequence is: hydroxyls ≅ carboxyls > amides > imides > ester > ether bonds. This isotherm section (up to $p/p_0 = 0.3$) is characterized by deep structural changes and chain extention. It is confirmed by IR-spectra in the Amide-I absorption region and by high values for the system's thermal heat capacity due to hydrogen bond rearrangements.[8]

The next section of the isotherm is more gentle. In the 0.25–0.55 interval of relative vapour pressure, water condenses in clusters in the vicinity of the hydrophobic parts of the polymer chain. Sorption heat decreases down to 44 kJ/mole, the value corresponding to the evaporation heat of water. This fact testifies to the preferability of interactions in water-water system. In the same region free water becomes apparent. Its quantity was determined by the DSC method.[9]

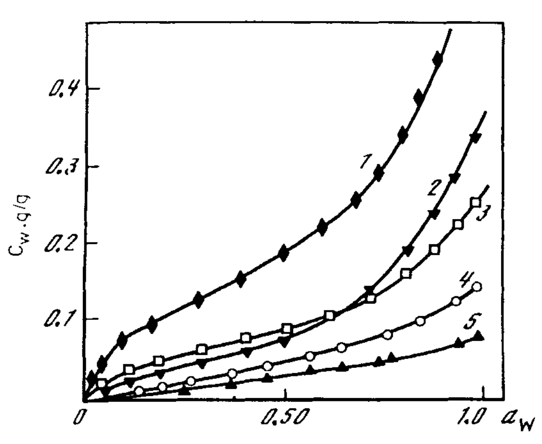


FIGURE 4 Water sorption isotherms of hydrophilic (collagen (1), PVA (2), keratin (3)) and moderately hydrophilic (acetate cellulose (4), Nylon-6.6 (5)).

Later associates begin to merge because of a continuous increase in the free water content of the polymer. Water's affinity with polar polymer groups is not a motive force for dilution, but rather entropy of mixing. Thus dilution could be more complete except for the limiting force of the polymer network. Elastic forces appearing as a result of network tension grow with the increase in the polymer's crosslink level. The latter increases as the sorbed water content decreases. This fact leads to isotherm changes in the region of high humidity.

The total course of the sorption curve also shows three characteristic sections: 1) 0–30% of H_2O in the sample—weak increase of probe mobility, fast rotation does not occur because of strong immobilization by the polymer chains and the absence of free water (the region of functional group hydration); 2) 30–60% H_2O—sharp increase in probe mobility because of polymer plastification and the appearance of free water (the region of coformation changes); 3) 50–70% and higher when the probe mobility reaches its maximum value in the swelled matrix (the region of gel existence).

WATER DIFFUSION IN HYDROPHILIC POLYMERS

The concentration dependence of the water diffusion coefficients in hydrophilic polymers is most often approximated by exponential functions. A sharp increase in the diffusional parameters is caused by significant changes in the polymer structure and an increase in nonbound water content in the polymer. Structural changes occur in such a way that the increase in frequency and amplitude of polymer segment mobility could take place under isothermal conditions. For glassy polymers, PVA for example, the phase transition of the second type occurs during the process of sorption and a highly elastic state is obtained.

With low water content in the external phase a hydrophilic polymer sorbs water in concentrations characteristic of hydrophobic samples. The presence of polar and ionogenic groups in the polymer matrix changes radically the transition mechanism as compared with that of hydrophobic polymers. Strong immobilization of water molecules at highly polar groups as well as braking of segmental mobility lead to low diffusion coefficients, namely 10^{-10}–10^{-11} cm^2/sec. For comparison: hydrophobic polymers with a low content of crystalline phase have much higher D_w: from 10^{-7}–10^{-9} to 10^{-5} cm^2/sec (polysiloxanes).

The solution of the direct diffusional problem, i.e., determination of $C(x, t)$ dependence from the initial conditions and the known type of function $D(C)$ was made with the help of an iteration algorithm.[10] For example, calculation of diffusion into a half-infinite medium was made for a PA-6-water system, where the concentration dependence of the diffusion coefficients is described by the equation

$$D = D_0 \exp(\lambda_i C) \qquad (15)$$

where $\lambda_i = \lambda_0 + i\Delta\lambda$, $\lambda_0 = 0$, $i = 1, 2, \ldots, 20$, λ_i changes in the interval 0–4; $D_0 = 1, 1$.

Figure 5 shows the distribution of water in a polymer for several specific λ_i

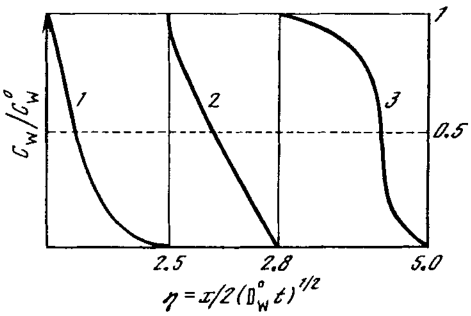


FIGURE 5 Distribution of water in polyamide in accordance with Equation 14 (λ = 4, 1 − i = 2, 2 − i = 15, 3 − i = 50).

values. As can be seen, when the concentration dependence of D_w is weak the curve of water concentration decreases through the sample thickness (reflected by the coordinate $\eta = x/[4D_{0i}]^{1/2}$) in a concave fashion. At intermediate λ_i values the dependence $C(\eta)$ is close to linear, while for a strong dependence of $D(C)$ the concentration profile in the polymer is stepped (see Figure 5). This coincides well with the results of the indication method, which also demonstrates a sharp border for polyamide-6 dying.[3]

The diffusion coefficient values of a binary system under investigation can be defined from the family of $C(\eta)$ curves, constructed with the help of the Statgraf 2.6 IBM PC/AT program.

The calculated D_w values of PA-6 at different temperatures are shown below. The temperature dependence of the diffusion coefficient is approximated by the classical Arrhenius equation.

T, °C	23	37	51	69
$D_w[10^{-8}]$, cm²/s	0.15	0.40	0.92	2.55

The adduced values of D_w and the diffusion activation energy $E_D = 54.3 \pm 1.3$ kJ/mole agree well with the sorption method data published in Reference 3. It permits one to consider the suggested method of definition and calculation of diffusional parameters as rather suitable for hydrophilic polymers.

For polymers with a high water content (gels), diffusion coefficient dependence on concentration is defined by that portion of the free moving water molecules shielded from polymer molecules by hydrating water. As in weakly linked hydrogels only some volume percent belongs to the polymer, whereas the linked water portion forms from $\frac{1}{4}$ to $\frac{1}{3}$ of the total for a variety of polymers. It is quite probable that continuous water regions should exist in the polymer matrix, through which free water migration takes place. Macromolecules, beginning from a certain concentration, can influence the process by steric factors leading to polymer network bypassing by the diffusing water molecules. D_w values in this case are close to those of the free water self-diffusion coefficient.

WATER DIFFUSION IN MODERATELY HYDROPHILIC POLYMERS

One difficulty with the above classification is created by polymers of intermediate type, which can show features, characteristic of either hydrophilic or hydrophobic polymers, in their dependence on the concentration of low molecular weight diffusional components. For such polymers a balance of dispersional and polar interactions is realized, and it determines the structure and morphology of the polymeric bodies and their ability to sorb water.

Some polymers of moderate polarity, for example polyvinylacetate, are characterized by a compensative effect, when immobilization and plastification influence water mobility in opposite ways. Because of this compensative effect the concentration dependence of D_w either is absent, or the function $D_w(C_w)$ increases, but less sharply than an exponent (linear or parabolic $\sim C_w^2$) as, for example, in cellulose acetate, containing 39.9% of acetic groups[11]

$$D_w = D_0[1 + k_1C_w + k_2C_w^2]. \tag{16}$$

In Reference 12 for epoxy resins the superposition of plastification and immobilization near polymer polar groups is seen. That leads to an extreme effect on the water diffusion coefficients. In Reference 13 a comparatively weak (nearly linear) concentration dependence of D_w for aromatic polyamides was discovered. The diffusion mechanism was defined by water molecule distribution in accordance with the Flory-Huggins equation and reversable linking at the immobilization centers.

A rather recently synthesized class of polymers (segmental polyesterurethanes (SPEU))—attract great attention thanks to pecularities of their chemical structure and morphology. The alternation of soft (polyester) and hard (polyurethane or polyurethaneurea) segments permit construction of different supermoleculear structures, including domains, owing to which these polymers show unique mechanical[14] and biological (biocompatible)[15] properties.

Sorption and especially diffusion of small molecules can be used for studying the structure and morphology of polymers. This method, in sensitivity, does not yield to such traditional structure-sensitive methods as microscopy, DSC, etc. In the ideal a combination of diffusional and, for example, spectroscopic methods significantly enlarges the information about the polymer structure's organization. That is why the right question is not about the contrast of the diffusion-sorption methods with other structure-sensitive methods, but about their being mutually complementary.

SPEU usage in biomedicine as materials for prosthetic organs and their components (prosthetic heart ventricles, clapans, diaphragms, catheters, etc.) demands a scientifically based system be created to control the materials and article applications. A condition for effective functioning of an article is its capability to perform (imitate) certain functions of the organism's biomedium not induce rejection by the organism and not damage the metabolic processes.

The main applications of prosthetic organ synthetic elements should be the capability for work and hemocompatibility. Real biological media, and models which imitate their behaviour, should be considered as a specific aggressive medium, water being its prevailing component. Water is a good plasticizer, decreasing T_{gl} and the modulus of elasticity in comparison with the glassy state.

In the presence of water a 15% increase of the dynamic modulus of transverse elasticity is observed (the effect exceeds the average measurement error by 6–8 times) due to 2.7% water absorption by SPEU samples at temperatures below the T_{gl}. Such a change in the modulus of elasticity as a result of water sorption is a typical antiplastification indication.[16] It is important that in this case the α-relaxation maximum is not displaced. Temperatures of the α- and γ-transition completion (221 ± 1 K° and 275 ± 3 K° correspondingly) also do not change. An increase of G' in the presence of water is accompanied by an α-relaxation peak amplitude in the $tg\delta(T)$ dependence two-fold increase in the preservation of γ- and α′-maxima of mechanical loss levels.

Thus, even a small quantity of water localized in the polyester phase (less than 1%) may be the cause of significant changes in the physical mechanical characteristics of materials in the oligoester glassy region. The most important to point out is that water's influence is defined by simple plastificating or nonplastificating action. The increase in the $Tg\delta$ parameter is evidently stipulated by hydrogen bond destruction at the border of the hard and soft domain structures and, consequently, leads to an increase in the kinetic element number taking part in microbrownian motion under α-relaxation in the absence of a visible plastification effect. The last indicates, that water molecules do not penetrate into domain structures (their existence is confirmed by DSA and TEM methods, but are concentrated in the transition layer, the accessibility of which is significantly higher in comparison to that of the domain.

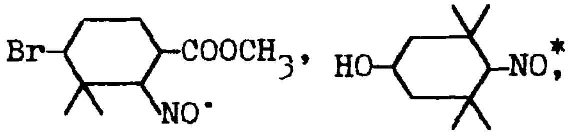
Moreover, the destruction of and the decrease in the number of hydrogen bonds in the system permit the realization of a much higher macrochain density in the processes following the transition from the highly elastic state into the glassy state.

The existence of a regular domain structure for SPEU samples with the commercial name "Vitur" (SPT Vladimirskoe), are registered by some independent methods (ESR, X-ray analysis, TEM, etc.).

The domain character of the polymer matrix under investigation permits one to suppose, that in the most general case the total water quantity in three different polymer zones is summed up by concentrations in the soft oligoester matrix C_w^e, in the hard phase C_w^u and in the intermediate interphase layer C_w^i

$$C_w^{\Sigma} = C_w^e + C_2^u + C_w^i.$$

Water dissolubility in the polyester (polytetramethylene oxide) matix is rather low and equal to fractions of a percent.[17] With the help of a measurement of organic and inorganic electrolyte penetrability, and also by recording the ESR-spectra of probes of the following structures:



introduced into SPEU, it was shown that water does not penetrate into the hard domain phase. The *H-D*-exchange appeared to be the most convenient means of domain structure estimation as the ester fragments and the elongators forming the SPEU chain are incapable of *H-D*-exchange whereas the *H*-atoms of the urethane and urea groups and the amide residues can be exchanged for deuterium. These groups are accessible to water molecules and the fact is confirmed by the degree of exchange, which is close to 0.25 for "Vitur-T0533" samples at 25°C. It means that $\frac{3}{4}$ of the urethane groups are shielded from contact with water molecules.

Hence, accommodation of water molecules in the polymers under investigation may be provided by the polyester links, the surface groups of the domains exposed to the soft phase, and the hydrophilic urethane and urea groups, included in the intermediate layer. The two last items play the most significant role as water dissolution in aliphatic and aromatic polyesters is rather low.

The sorption heat value, being close to 0 in the SPEU-water system, testifies to the weak interaction of water with the methylene and ester groups of the soft phase, from one side, and from the other to a certain compensation of the rupture energy of the hydrogen bonds (—NHCO— . . . HOH) also observed for amide groups in polyamides.

The positive deviation of sorption from the Henry isotherm was considered with the help of the associative model described in the previous part. Equation (5), with appropriate constants (K_H, K_T, N_c), helped to describe satisfactorily the experimental results. This fact testifies to the partial immobilization of water molecules by the urethane and urea groups.

The decrease of the effective diffusion coefficients D_w of water in SPEU along with the increase in the relative humidity also is a characteristic indication of diffusing molecule immobilization. The concentration dependence of D_w was described in accordance with the partial immobilization model (Fig. 6).

Figure 7 shows equilibrated water content in polyurethaneacetals, formed through the connection of divinyl ester of diethyleneglycol to urethane glycols and polyethyleneglycoladipate in various ratios depending on the degree of structure regulation.[18] It can be seen that hydrophilic and moderately hydrophilic polymers are characterized by a proper set of parameters in equation

$$\alpha_w = \alpha_w^0(1 - \alpha_k)^a, \qquad (17)$$

where α_w^0 and α_w are the characteristic parameters of polyurethane sorption.

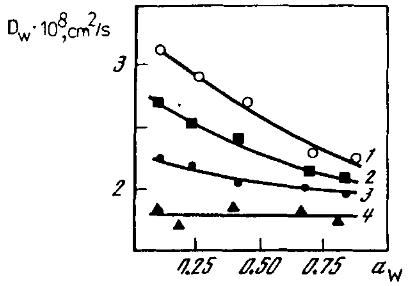


FIGURE 6 Concentration dependence of D_w for segmented polyetherurethane with concentrations of rigid segments are 48% (1); 34% (2); 27% (3); 21% (4).

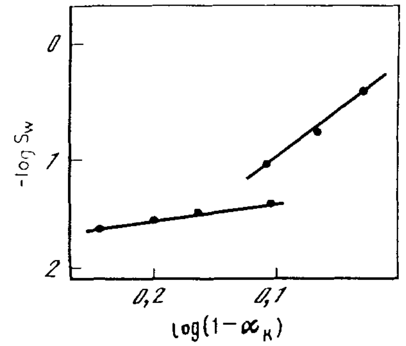


FIGURE 7 Dependence of water solubility in polyurethanes (S_w, g/g) on crystalline degree of specimens.

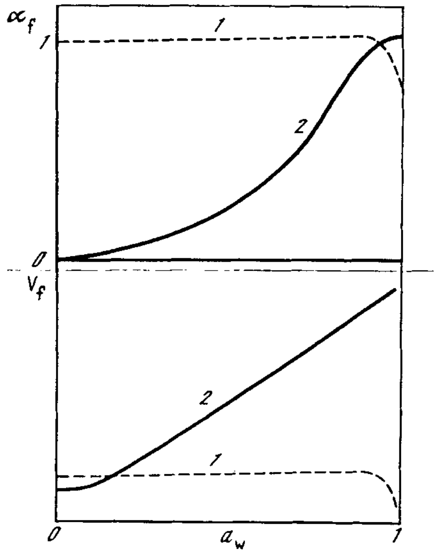


FIGURE 8 Representation of concentration dependence for mobil molecules fraction (α_f) and free volume (V_f) in systems hydrophobic polymer—water (1) or hydrophilic polymer—water (2).

Moderately swelling polymers show a square dependence of the content of amorphous phase on the equilibrium water absorption. This is in good accordance with the Mackay-Mears theory considering steric effects on position and diffusion of low-molecular weight components in polymers. For hydrophilic polymers the power in Equation (16) is significantly higher ($n = 5$), stipulated by a strengthening of water molecule interactions with polyurethane polar groups. Water content in the amorphous phase is also higher for hydrophilic polyurethaneacetals, than for moderately hydrophilic ones.

Hence, the division of polymers into hydrophilic, hydrophobic and moderately hydrophilic is stipulated not by total water absorption but by the method of water molecule immobilization (placement) in the polymer matrix and by the appropriate values for their diffusion mobility. Obviously, this thesis should be illustrated by a generalized scheme (Figure 8) which demonstrates the principle difference in the diffusion-sorptional behaviour of polymers of various hydrophilicities.

A significant decrease in the degree of water immobilization in a hydrophobic matrix at T = const., (defined as $C_f/C_w = \alpha_f$), and a practically constant free volume V_f fraction at high water activities is observed as part of the water is bound in associates and clusters. On the contrary the increase in α_f and V_f in hydrophilic polymers follows from a complicated process of plastification and hydrogen bond redistribtion characteristic of hydrophilic polymer system. The linear character of the free volume increase in swelling materials corresponds to the Yasuda model and defines the exponential increase of the diffusion coefficients for water concentration in the polymer. The superposition of the effects of plastification and immobilization in associates for polymers of intermediate hydrophilicity may manifest itself as an external dependence of diffusion parameters on water concentration.

Acknowledgment

The authors are thankful to Dr. L. Razumovskii, Dr. A. Polishchuk, Dr. A. Samoilenko and Dr. O. Startsev for providing laboratory facilities and fruitful discussion.

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