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Interrelation between Structural-Morphological and Diffusion-Kinetic Processes in Polymers with Different Hydrophilicity Degrees

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Quantitative analysis of diffusion of mineral (HCl, H₂SO₄, HNO₃) and organic (HCOOH, CH₃COOH, C₂H₃COOH) electrolytes both in hydrophilic (poly(vinyl alcohol) and moderately hydrophilic (Nylon-6, Nylon-6,6) polymer membranes is made. Structural changes in the polymer matrix accompanying diffusive transport and affecting its rate are studied by X-ray structure analysis at wide and small angles. A diffusion model taking into account morphological changes in polymers with different hydrophilicity degrees is proposed and the interrelation between diffusion and structural characteristics is demonstrated.

KEY WORDS Polymer membranes, diffusion, structure, organic acids, inorganic acids, hydrophilicity.

The theory and practice of membrane technology are based on studies of diffusion phenomena since these phenomena mainly determine the mechanisms of separation, purification, and concentration of electrolytes using polymer membranes.^{1–4}

At present, the interrelation between the polymer structure and the kinetics of diffusion processes in materials with different hydrophilicity degrees has been considered in a very limited number of works,^{1,5,6} which hinders the evaluation and prediction of the behavior of diffusion systems whose structure is capable of undergoing evolution in time (dialysis systems, polymeric depots of pharmaceuticals, membrane detectors for environmental monitoring, and so forth).

Our studies are concentrated on moderately and highly hydrophilic polymers whose behavior on contact with solutions of electrolytes may differ noticeably. It is under these conditions that hydrophilic polymers manifest their specific features⁵; in moderately hydrophilic polymers characterized by rough compensation of hydrophilic-hydrophobic interactions between their structural elements (hydrophilic-hydrophobic balance) fine structural transitions are possible, while in highly hydrophilic polymers structural changes can occur at all levels (chemical-polymer analogue transformations, crystal structure-decrystallization and additional crystallization, changes in porosity, melting of domains).⁷

The purpose of this work is a quantitative analysis of the diffusion of aqueous solutions of electrolytes with allowance for the structural features of hydrophylic poly(vinyl alcohol) and moderately hydrophilic (PA 6, PA 6,6) polymers.

MATERIALS AND METHODS

Poly(vinyl alcohol) (PVA) (Poval-220, Japan and a Soviet product) and polyamide (PA 6, PA 6,6, Bayer, FRG) films are used in the experiments.

The structure of the films (humid and dry) is studied using X-ray diffraction at large (LAD) and small (SAD) angles.^{8,9}

The permeability of polymer membranes is investigated on an original unit whose major component is a dialysis cell described earlier¹⁰ and is characterized by the following parameters: $V_1 = 90 \text{ cm}^3$ (working volume), $S = 0.785 \text{ cm}^2$ (working area of the membrane), $R = V_1/S = 115 \text{ cm}$ (cell constant).

Chosen as diffusing agents are water and aqueous solutions of inorganic (nitric, sulphuric, hydrochloric) and organic (formic, acetic, propionic) acids. All the reagents (chemically pure grade) are diluted with twice distilled water to a concentration of 0.05 N–1 N. The rate of diffusive transport is determined by measuring the flux of the diffusing substance in terms of permeability:

$$P = (dC/dt)Rl$$

where dC/dt is the stationary change in the concentration of the substance transported across the polymer film, R is a linear characteristic parameter of the diffusion cell, and l is film thickness.

RESULTS AND DISCUSSION

1. The structural-kinetic aspect of interaction of electrolytes with hydrophilic polymers

Commercial PVA specimens (films) prepared by casting from aqueous solutions contain crystalline, paracrystalline and amorphous areas in different proportions.¹¹ The specimens under study are characterized by the predominance of a paracrystalline structure. LAD patterns with sharp 4.5 Å and 2.2 Å reflections are observed in this case (Figure 1a), which testifies to the presence of areas with a dense packing of parallel isolated chains with a random azimuthal turn of each chain with respect to the neighboring chains.¹²

It was shown earlier¹³ that two parallel structural processes take place in the course of water sorption by PVA films: a relatively fast process (seconds) of moving the polymer chains apart by the molecules of water penetrating between them, and a slower process (minutes) of the transition of the paracrystalline structure of PVA into the crystalline structure. The fast process is tracked by the decrease in the intensity of the 4.5 Å reflection, and the slow process by the growth of the intensity of the 3.9 Å reflection (Figure 1a) characterizing only the crystalline structure.

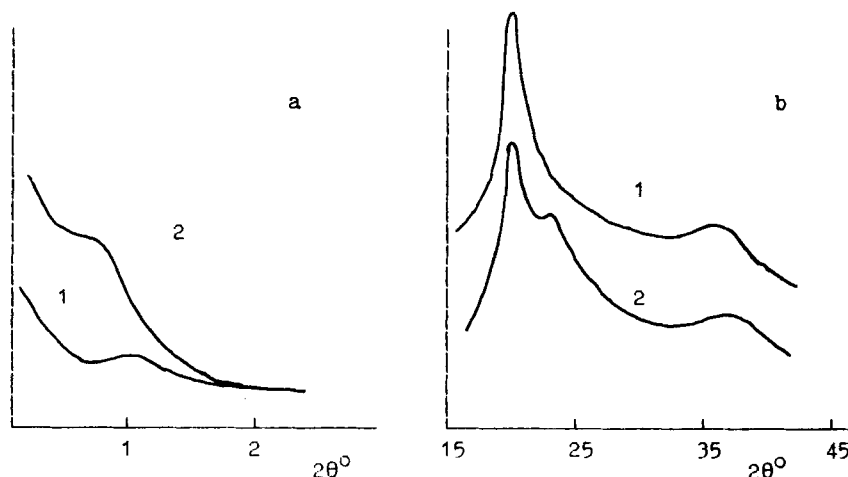


FIGURE 1 Large-angle (a) and small-angle (b) X-ray diffraction patterns of dry (1) and 50% humid (2) PVA films (for the convenience of visual presentation, the curves in Fig. 1a are arbitrarily shifted along the y axis).

During water desorption, the initial paracrystalline structure restores, as is evidenced by corresponding LAD patterns.

SAD patterns of dry PVA films (Figure 1b) reveal a weak reflection corresponding to a spacing of 90 Å and caused by a regular alternation of more ordered and less ordered areas of lamellar or fibrillar structures. Irregular alternation of areas with different electron densities is known to give a diffuse scattering background on SAD patterns. Therefore, the larger the background intensity of X-ray patterns, the more inhomogeneous (heterogeneous) is the structure of the polymer. It can be seen from SAD patterns that the homogeneity of PVA films in a dry state is very high. Water sorption by the films under study increases the intensity of the diffuse background of SAD patterns, thus testifying to the growth of the heterogeneity of the structure at the level of colloid size. Upon drying, the initial SAD patterns restore; this means that the development of heterogeneity at the colloid level in PVA films is a reversible process.

Consider the extent to which the nature of the polymer matrix affects the diffusive transport of water and aqueous solutions of electrolytes. For hydrophilic polymers at temperatures not far from the glass-transition temperature, the relaxation times of polymer segments are comparable with or larger than the characteristic times of diffusive transport of the components of solutions ($\Theta = l^2/D$). In view of the reversible character of the change of the structure of the polymers under study, it is thought that the process of water transport can be described by the equation

$$\partial C_w / \partial t = \partial / \partial x (D_w \partial C_w / \partial x) \quad (1)$$

where D_w and C_w are the diffusion coefficient and concentration of water in the

polymer, respectively, with boundary conditions

$$C_w(0, t) = C_w^0 + (C_w^0 - C_w^\infty)(1 - e^{-kt}) \quad (2)$$

where C_w^0 , C_w^∞ are surface concentrations at $t \rightarrow 0$ and $t \rightarrow \infty$, k is the effective constant characterizing the average relaxation time of macromolecules and l is membrane thickness.

Using the infrared ATR technique, we showed in our earlier studies that the surface concentration of water in PVA specimens (in a layer 0.6 μm thick) did not reach the constant value immediately, the process being described by the equation¹⁴

$$\log_e((C_w^\infty - C_w^0)/(C_w^\infty - C_w)) = kt. \quad (3)$$

The solution of equation (1) as such with asymmetrical boundary conditions (2) specifying the exponential growth of the surface concentration is^{5,15}

$$\Theta/l^2 = (6D)^{-1} + (1 - C_w^0/C_w^\infty)(kl^2)^{-1}. \quad (4)$$

This expression describes the dependence of the time lag Θ , determined in permeability experiments (Figure 2) on the thickness of the specimen. The transport parameters of water and acids (which obey the laws indicated above) in the hydrophilic polymers under study are listed in Table I, which shows that the processes of molecular relaxation play an essential part in nonstationary diffusion of water and aqueous electrolytes into hydrophilic polymers since changes in the conformations of macromolecules, in the first place, are due to the interaction of the components of electrolytes with macromolecules.

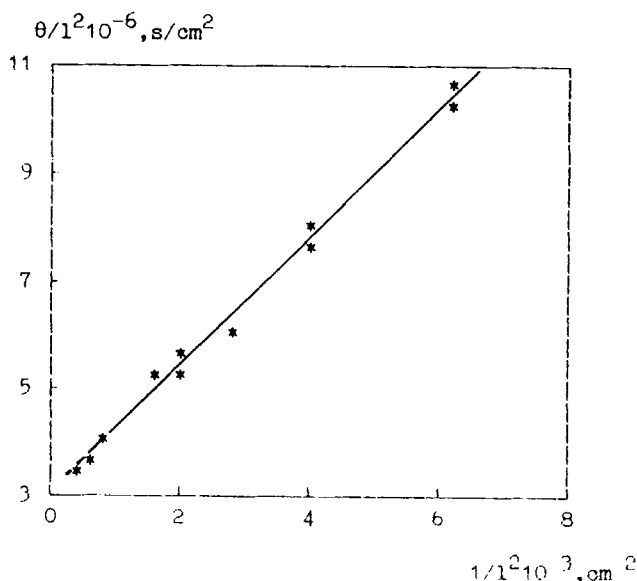


FIGURE 2 Dependence of the reduced time lag Θ/l^2 on squared inverse thickness $1/l^2$.

TABLE I

Parameters of nonstationary diffusion of organic acids in PA6 and PVA for 51- μm thick films

System	$\Theta 10^{-3}$, s	$1/kI^2 10^{-8}$, cm^2/s	$D 10^8$, cm^2/s	C_s , kmol/m^3
HCOOH—PA6	0.81	0.06	1.73	4.12
CH ₃ COOH—PA6	2.04	0.51	0.67	0.74
C ₂ H ₅ COOH—PA6	2.64	0.43	0.40	0.67
HCOOH—PVA	0.31	0.014	200	1.18
CH ₃ COOH—PVA	0.71	0.059	180	1.58
C ₂ H ₅ COOH—PVA	0.83	0.10	170	0.91

A detailed investigation of the interrelation between the structural and transport characteristics inherent in moderately hydrophilic polymers is carried out on systems polyamide 6—aqueous solutions of mineral acids.

2. A diffusion model of transport of inorganic acids in structurally heterogeneous moderately hydrophilic polymers

Real polyamide specimens may contain several structural components: two stable crystalline forms α and γ , unstable paracrystalline (imperfect) α^* and γ^* forms structurally similar to them and amorphous fractions.¹⁶ Under the action of water or aqueous solutions of electrolytes, unstable α^* and γ^* forms gradually transform into the α form.⁹

This structural rearrangement labeled by Machulis and Tornau¹⁷ as γ - α crystal transition is observed upon treatment of polycapraamide PK-4 films with inorganic acids.

The kinetic scheme of the crystal transition given by Machulis and Tornau¹⁷ does not take into account diffusion of the acid, and the suggested unit event of interaction of the acid with the polymer is purely formal since the chemical reaction and the transport of the acid in the crystalline phase are not feasible in reality. From our point of view, the unit event of this interaction is the rupture of hydrogen bonds between the amide or terminal groups accompanied by the transport of the molecules of the acid in the mesomorphous (low-ordered) area. The same event seems to initiate structural $\gamma^* \rightarrow \alpha$ and $\alpha^* \rightarrow \alpha$ transitions starting with the boundary layer or less accessible volumes of the structure.

Such terms as the structure of the amorphous and mesomorphous areas are accepted in the literature dealing with diffusion in polymers. Unfortunately, these terms do not fully fit the crystallographic concepts of the paracrystalline and amorphous fractions.

The following conventions are made in discussing PA diffusion data: the term amorphous phase refers to the areas where only diffusion of the electrolyte occurs and the process of rupture of H bonds does not take place; the term crystalline phase, to the areas where there is no transport of the components of the electrolyte; the term mesomorphous phase, to the areas where diffusion is accompanied by the reaction of rupture of interamide hydrogen bonds.

Figure 3 displays the dependence of the concentrations of the acids under in-

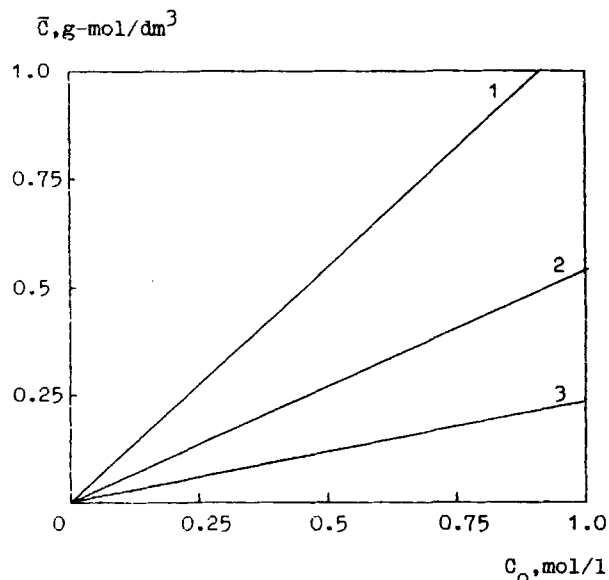


FIGURE 3 Dependence of equilibrium concentrations of acids in PA 6 on their level in aqueous solution: (1) HNO₃; (2) HCl; (3) H₂SO₄.

investigation in PA 6 (containing predominantly the γ^* structural form under initial conditions) on their concentrations in the solution. The concentration range indicated (0.1–1 mol/dm³) corresponds to the amide sorption region. It can be seen that all dependencies of C_s on the concentration in the solution are linear, which testifies to the invariability of the corresponding distribution coefficients K . In polyamide 6 the acid features equilibrium distribution between the amorphous and mesomorphous areas without affecting the crystalline areas:

$$C_s = C_a + C_m = K\bar{c}_0 \quad (5)$$

where C_s and \bar{c}_0 are concentrations in the polymer and solution, respectively, and C_a and C_m are concentrations in the amorphous and mesomorphous areas of PA 6, respectively, with reference to the unit volume of the whole polymer.

Equilibrium of the acid between the amorphous and mesomorphous areas is established following the reaction:



where HA is the molecule of the acid located in the amorphous or mesomorphous m phase, Θ is the sorption site characterizing the mesomorphous area and K_m is the equilibrium constant.

Taking into account equation (5) and reaction (A), the surface concentrations

in the amorphous (C_{a0}) and mesomorphous (C_{m0}) areas are related to the concentration of the acid by the following dependence:

$$C_{i0} = \frac{1}{2} \{Kc_0 \mp A_0 \mp (1/K_m) - [Kc_0 - A_0 - K_m^{-2} + 4Kc_0/K_m]^{1/2}\} \quad (6)$$

having the + signs if $i = m$ and the - signs if $i = a$; A_0 is the initial concentration of the immobilization sites.

The specific features of the transport of nitric, hydrochloric and sulphuric acids across PA 6 membranes are studied by making a comparative analysis of their permeabilities. Figure 4 presents the concentration dependencies of the permeability to HNO_3 before and after a prolonged treatment of the polymer with the acid (4 h; further treatment did not alter the shape of the $P(c_0)$ curve). Starting with certain concentrations in the solution, both dependencies are described by straight lines of the form $P = ac_0 - b$ ($a > 0, b > 0$), the slopes of the lines being virtually identical and the intercept on the x axis decreasing after polymer pretreatment with the acid. Similar curves are obtained on membranes of different thicknesses (Figures 5 and 6) both for HNO_3 and HCl . These results suggest that at high concentrations in the solution, the acid is transported across the film at a constant rate. The retardation of the transport process at comparatively low concentrations is a function of the history of the specimen (type of pretreatment) and of membrane thickness.

Let us now analyze the linear portion of the $P(c_0)$ curve as applied to concrete experimental conditions (equation (7)).

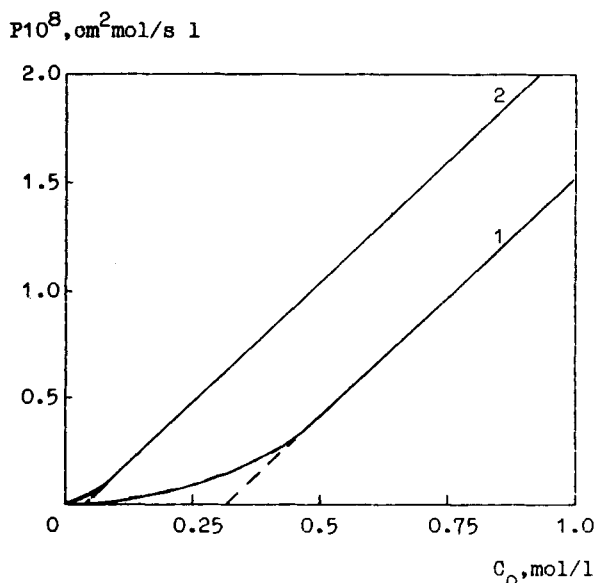


FIGURE 4 Concentration dependence of HNO_3 penetration into PA 6 (1) before and (2) after polymer treatment with the acid (4 h, $C_0 = 1 \text{ mol/l}$); $l = 53 \text{ }\mu\text{m}$.

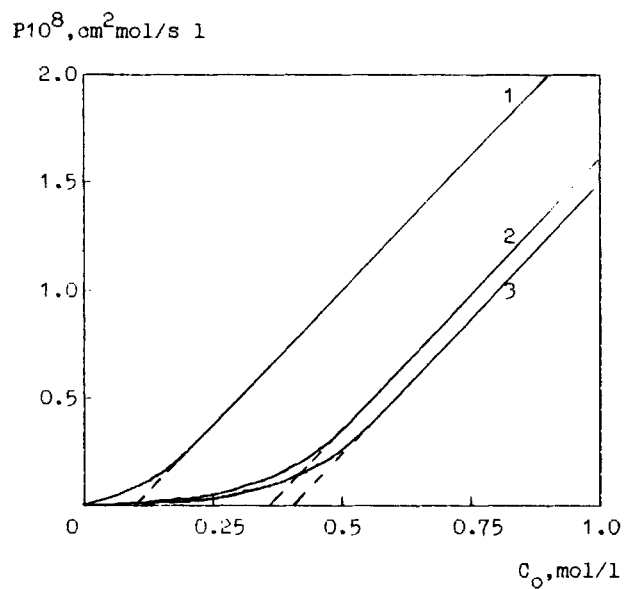


FIGURE 5 Concentration dependence of HNO_3 penetration into PA 6 at film thicknesses of (1) 24; (2) 53; (3) 100 μm .

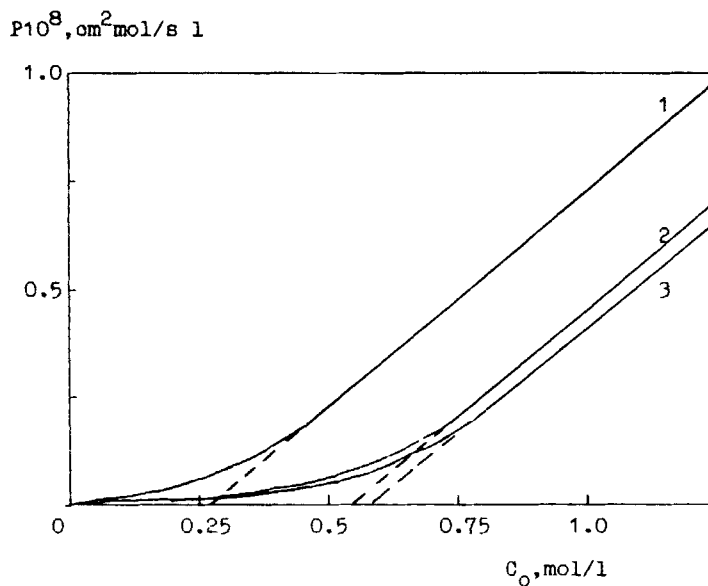


FIGURE 6 Concentration dependence of HCl penetration into PA 6 at film thicknesses of (1) 24; (2) 53; (3) 100 μm .

Assuming the constancy of the diffusion coefficients in each phase, permeability can be expressed as

$$P = D_a C_{a0} + D_m C_{m0} \text{ or } P = D_a K C_0 - (D_a - D_m) C_{m0}. \quad (7)$$

It is evident that equation (7) represents the linear portion of the experimental curve under the condition that $C_{m0} = \text{const.}$ (independent of the concentration of the acid in the solution), assuming the obvious $D_a \geq D_m$.

An analysis of the results of the interaction of the acids with polyamides indicates that the diffusion model of transport should take into account the following major features:

1. Equilibrium at the polymer/solution interface is established following equation (6).
2. The concentration of the acid in the mesomorphous area has a limit which is independent of its concentration in the solution.
3. The transport of the acid in the mesomorphous phase is accompanied by an irreversible reaction of rupture of hydrogen bonds between amide groups.

In view of these features, the transport of the acid in the amorphous area is described by the equation

$$\Sigma \partial C_a / \partial t = D_a (\partial^2 C_a / \partial x^2) \quad (8)$$

where D_a is the diffusion coefficient of the acid in the amorphous area.

In the mesomorphous area the transport is accompanied by the reaction of rupture of hydrogen bonds:



(k_H is the rate constant of the reaction) and is described by the equation

$$\partial C_m / \partial t = D_{0m} \partial^2 C_m / \partial x^2 - k_H C_m C_{\text{NHCO}} \quad (9)$$

where D_{0m} is the diffusion coefficient in the mesomorphous area.

It should be noted in connection with equation (9) that stationary transport in the mesomorphous area is only possible under the condition that $A_{0m} \gg [\text{NH}_2^+ \text{COA}^-]$, where $A_{0m} = [\text{NHCO}]_{t=0}$ is the initial concentration of amide groups linked via hydrogen bonding.

Thus, under our experimental conditions the stationary transport of the acid

across PA 6 is described by a set of equations (8) and (9) with the following boundary conditions:

$$C_a(0, t) = C_{a0}, \quad C_a(x, 0) = C_m(x, 0) = C_a(l, t) = C_m(l, t) \\ = 0, \quad C_m(0, t) = C_{m0}, \quad C_{a0} + C_{m0} = kc_0, \quad k = k_H A_{0m}.$$

The solution of this set provides the following expressions for the stationary flow:

$$J = D_a C_{a0} / l + (D_{0m} k)^{1/2} C_{m0} / \sinh[(K/D_{0m})l] \quad (10)$$

and permeability to the acid:

$$P = D_a k c_0 - D_a (1 - D_{0m} y / D_a \sinh y) C_{m0} \quad (11)$$

where $y = (kl^2/D_{0m})^{1/2}$, $C_{m0} = K_m A_0 C_{a0} / K_m C_{a0} + 1$ ($y/\sinh y$ is a decreasing function of the variable y with $\lim_{y \rightarrow 0} y/\sinh y = 1$, $\lim_{y \rightarrow \infty} y/\sinh y = 0$).

Consider Figure 4, which displays the concentration dependencies of permeation of the acid into the films after different types of treatment. It is clear that preliminary soaking of the films in the acid reduces such parameters as A_{0m} , k , y and therefore raises permeability, as evidenced by Figure 4.

An increase in the thickness of the membrane (Figure 5) lowers, as follows from the foregoing, the effective diffusion coefficient in the mesomorphous area $D_m = D_{0m} y / \sinh y$, as manifested in lower values of the permeability y of thicker films. In Figure 6 the shift of the permeability curves on the x axis leads to a limit, as follows from the shape of the $y/\sinh y$ function. In physical terms, this means that beginning with certain l values, the transport of the acid across the mesomorphous area can be neglected, as indicated by the inequalities $y \ll 1$ and $D_m \ll D_a$, and the thickness of the membrane no longer affects the transport rate.

At $K C_{a0} \ll 1$ the character of the concentration dependence $P(c_0)$ changes, as is exemplified by the dibasic sulphuric acid (Figure 7). The permeability graph becomes linear:

$$P = D_a K c_0 (1 + K_m A_0)^{-1} (1 + [D_{0m} y / D_a \sinh y]) K_m A_0, \quad (12)$$

the permeability coefficient P_0 (the slope of the $P(c_0)$ line), decreasing with membrane thickness, as illustrated by Figure 7.

Using the diffusion model, one can determine experimentally all physicochemical parameters characterizing the acid/polymer system. By way of example, consider the diffusion of nitric acid into PA 6.

Denote the intercept of the asymptotes of the permeability curves on the concentration axis as C' . Consider now C' as a function of the membrane thickness (Figure 8) whose experimental values are known:

$$C' = (1 - D_{0m} / D_a [y / \sinh y]) A_0 / K; \quad y = y(l). \quad (13)$$

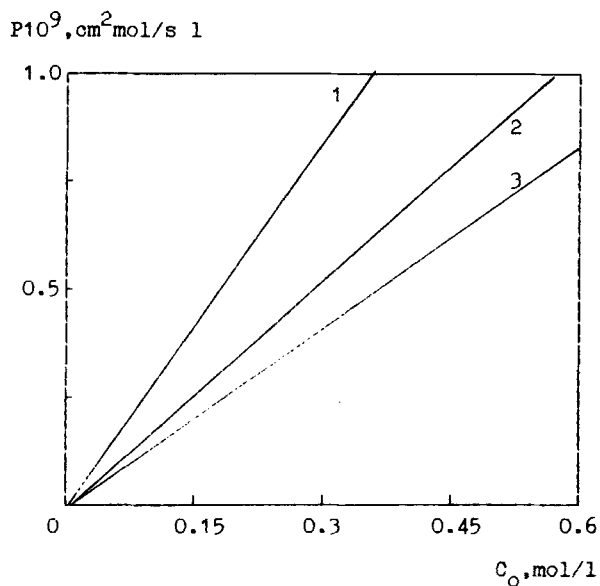


FIGURE 7 Concentration dependence of H_2SO_4 penetration into PA 6 at film thicknesses of (1) 24; (2) 53; (3) 155 μm .

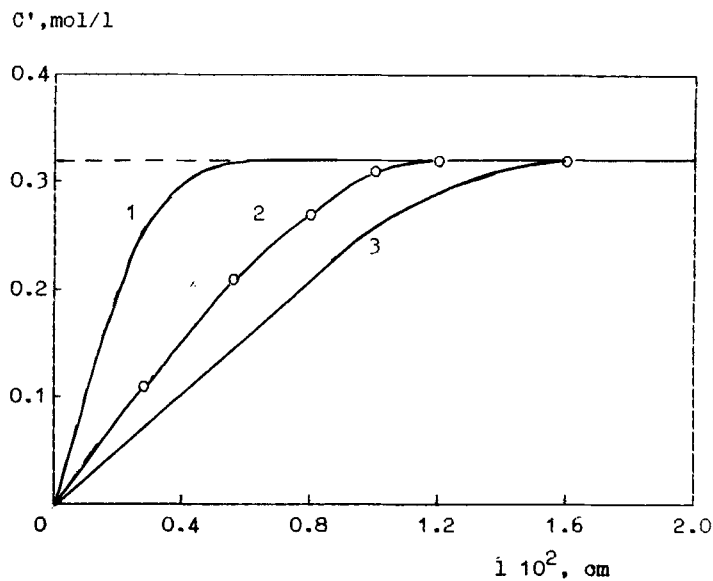


FIGURE 8 Comparison of calculated and experimental (points) dependencies of C' on membrane thickness at (1) $k \times 10^3 = 5$; (2) $k \times 10^3 = 3.6$; (3) $k \times 10^3 = 1 s^{-1}$.

Remembering that $y/\sinh y \rightarrow 0$ at $y \gg 1$, the ultimate value of C' is $C' = A_0/K$. The only unknown parameter determining the form of the functional dependence $C' [y(l)]$, viz. the effective rate constant of protonization of amide groups k is found by numerical analysis.

The tangent of the slope angle φ of the linear portion of the permeability curve is related to the diffusion coefficient of the amorphous area by the relationship $\tan \varphi = D_a K$; this makes it possible to calculate D_a . The values of the equilibrium constants k_m are determined using the permeability data for low concentrations, e.g., with the help of equation (12).

The transport parameters of the inorganic acids in PA 6 are listed in Table II.

An analysis of the data published in the literature does not clarify the mechanism by which diffusion of certain mineral acids and some other electrolytes occurring in noncrystalline areas of the polymer still leads to the $\gamma^* - \alpha$ structural transition in PA 6. It seems that our diffusion model that takes into account the structural-morphological features of the polymers under study¹⁸ helps to solve the problem.

Together with other authors,¹⁹ we think that the $\gamma^* - \alpha$ transition is promoted by mineral acids (HNO_3 , HCl , H_2SO_4 , and so forth); however, our standpoint is that the process involves the rupture and spatial redistribution of the hydrogen bonds of the polymer's amine and amide groups by the diffusing acid. The imperfect and energetically less favorable γ^* form cannot undergo a spontaneous transition into a more stable α form since it is stabilized by the surrounding segments of macromolecules not included in ordered structures, through H bonds whose saturation degree is very high. As we have already noted, diffusion-induced concentration of the electrolyte at the boundary between the ordered and unordered areas brings about the rupture and redistribution of hydrogen bonds in this boundary area. The appearance of the translational mobility of polymer segments in the ordered areas freed from hydrogen bonds hampering the movement of the macromolecules favors the transition to a more stable α form. By the way, the stabilizing hydrogen bonds can also be ruptured by applying temperature²⁰ or a mechanical force field.

The conversion from one structural modification to another requires the rupture of a certain critical number of hydrogen bonds; this means that due to diffusion, a certain critical concentration of the electrolyte capable of initiating the transition should be accumulated in the polymer. For PA 6 this concentration is equal to the concentration of amine end groups ($C_{cr} = 7 \times 10^{-2} \text{ mol/dm}^3$).

It has been shown experimentally that the kinetics of formation of the α form is described by a first-order equation^{9,19}

$$dC_\alpha/dt = AK_\alpha(C^0 - C_\alpha) \quad (14)$$

TABLE II
Parameters of transport of inorganic acids in PA6

Parameter	Nitric	Nitric acid*	Hydrochloric acid	Sulphuric acid
$D_a 10^8, \text{ cm}^2/\text{s}$	2.3	2.3	1.6	0.8
$D_{0m} 10^8, \text{ cm}^2/\text{s}$	1.7	1.7	0.6	0.6
$k 10^{-2}, \text{ s}^{-1}$	0.36	0	0.63	0.17
$K, \text{ dm}^3/\text{dm}^3$	1.08	1.08	0.58	0.22
$A_0, \text{ mol/dm}^3$	0.32	0.32	0.32	0.16
$K_m, \text{ dm}^3/\text{mol}$	3.0	3.0	3.0	3.0
D_{0m}/D_a	0.7	0.7	0.4	0.75

* A prolonged treatment of the polymer with the nitric acid for 4 h.

where C^0 is the concentration of the ordered phase of the polymer capable of the structural transition and C_α is the concentration of those polymer units that undergo transition to the α form.

Suppose, in addition, that the crystallites are uniformly distributed throughout the membrane thickness with a constant concentration C_{max} . In some cases that is not quite justified since the surface layers of sufficiently thick polyamide films differ structurally from the central part²¹; however, in our case we assume that the specimen is isotropic in order not to make the model much more complicated. Also, assume that the overall orderliness does not change, as suggested by the X-ray structure analysis data (Table III).

The following versions are possible in the course of diffusion of the acid into the polyamide film (sorption experiment):

A. At any X ($0 < X < l$), $C_m(X) \geq C_{cr}$; evidently, $C^0 = C_{max}^0$ and

$$C_\alpha = C^0(1 - \exp[-K_\alpha t]). \tag{15}$$

This version is discussed by Machulis et al.¹⁹

B. At any distance from the surface, X ($0 < X < l$), $C_m(X) < C_{cr}$; this means that due to a low diffusion rate or small boundary values of the concentration of electrolytes, its critical level in the polymer is not reached at any point. In this case $C^0 = C_\alpha = 0$.

C. In a more general case, the following conditions are satisfied in a certain point X in the polymer ($0 < X < \frac{l}{2}$):

$$C(X) = C_m(2l - x) = C_{cr};$$

$$C(x) < C_{cr} \text{ in the interval } X < x < l - x;$$

$$C(x) > C_{cr} \text{ in the interval } x < X \text{ or } x > l - x.$$

Then for one-dimensional diffusion, assuming a sufficiently sharp front, we have

$$C^0 = 2C_{max}^0 X/l; \tag{16}$$

TABLE III

Characteristics of structure taken from the data of small-angle X-ray diffraction of polyamide films before and after diffusion of water and 1 N nitric acid

PA 6 specimen	t_a^*	I_r	I_b	$d_m, \text{\AA}$	%	$R_d, \text{\AA}$
Initial, dry	0	1.0	1.0	63	52	14
Humid, 24 h in water		1.2	1.3	73	50	16
Same, dried		1.2	1.6	70	55	15
After 1 day in water	0.5	0.8	1.2	73	57	17
After 1 day in water	3.0	0.7	1.3	73	54	18
After 1 day in water	5.0	1.6	1.7	73	50	17

* Time of treatment with nitric acid h; the relative accuracy of determination of all parameters except d_m is not worse than 15%, that of spacing, d_m , determination $\approx 5\%$.

in view of $X = X(t)$, the solution of the differential equation is

$$C = 2C_{\max}^0 \exp[-K_{\alpha}t] \int_0^t K_{\alpha}X(\tau) \exp K_{\alpha}\tau d\tau \quad (17)$$

where τ is the integration variable.

The stationary distribution of the acid in the mesomorphous transition area surrounding the ordered areas in the polymer where the process of rupture of hydrogen bonds should be taken into account, can be described by solving the set of differential equations (8) and (9) for constant boundary conditions:

$$C(0) = C(l) = Kc_0;$$

$$C_m(x) = C_{m0} \cosh(K/D_{0m}[1/2 - x]^2) [\cosh(kl^2/4D_{0m})]^{-1/2}. \quad (18)$$

This equation makes it possible to derive an expression for X at $C(X) = C_{cr}$ and substitute it into equation (18), finally obtaining for stationary transport C_{stat} :

$$C_{\text{stat}}^0 = C_{\max}^0 \{1 - [4D_{0m}/Kl^2]^{1/2} \cosh^{-1}(C_{cr}/C_{m0}) \cosh(Kl^2/4D_{0m})^{1/2}\}; \quad (19)$$

and finally,

$$C_{\alpha} = C_{\text{stat}}^0 (1 - \exp[-K_{\alpha}t]). \quad (20)$$

Unlike equation (15), Version A, in this case C_{stat} depends on diffusion parameters, the rate constant of rupture of hydrogen bonds k and the geometry of the specimen.

An analysis of equation (19) shows that an increase in the dimensionless parameters $(Kl^2/4D_{0m})^{1/2}$ and C_{cr}/C_{m0} lowers the value of the transformation limit C_{stat}^0 and the rate of the structural transition. A comparison of the conclusions that follow from equation (19) with the results of measurements of the kinetics of the γ^* - α transition⁹ (X-ray data) demonstrates their good correlation. It can be seen from Figure 9 that the stationary limit of transformation into the α form grows with C_{0m} increasing (C_{0m} is the equilibrium concentration of the electrolyte at the polymer/solution interface). A conclusion that the hypothetical or real growth of the critical concentration of the acid in the layer bordering the crystalline areas should bring about a decrease in C_{stat}^0 seems to be well substantiated. Parameters such as the thickness of the specimen and the constant of the redistribution (rupture) of hydrogen bonds favoring immobilization of the diffusing acid also affect the stationary transformation limit. The effect of the nature of the acid manifests itself, in the first place, in the characteristics of the diffusion system (D_{0m} , C_{0m}) which exert positive influences on the rate of structural transformation.

It can be seen from Table II that nitric acid possesses the highest diffusion coefficient in the amorphous area, the D_a value being independent of the history of the specimen. In the course of polymer treatment with the acid the effective rate constant of protonization decreases, which is related to the lowering of the

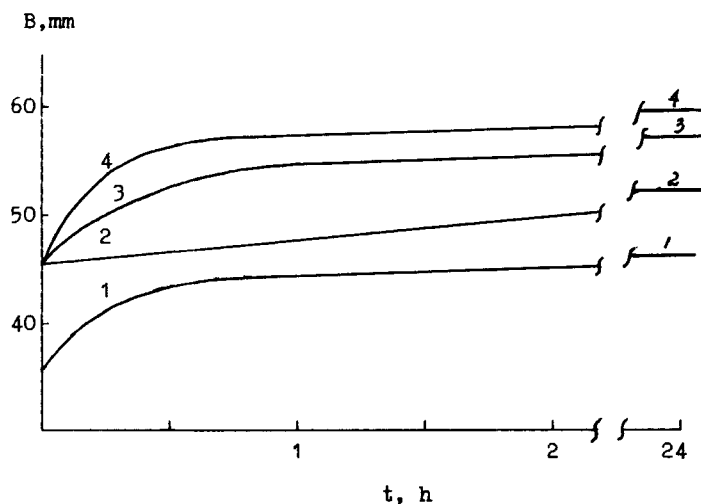


FIGURE 9 Dependence of the index of formation and perfection of the α^- structure B on the duration of action of (1) water; (2) 0.5 N; (3) 0.75 N; (4) 1 N nitric acid on $50\text{-}\mu\text{m}$ thick PA films. Prior to acid treatment, the films had been held in water for 24 h. B is the width of the main total reflection on the large-angle X-ray diffraction pattern at its half-height at $2\theta = 21.5^\circ$.

concentration of the amide groups linked by hydrogen bonds. Oxygen acids (nitric and sulphuric) are characterized by higher relative D_{0m}/D_a values and lower, as against HCl, rate constants of the rupture of hydrogen bonds. Parameters A_0 and K_m primarily characterize the properties of the polymer. The halved values of A_0 in the case of sulphuric acid are due, in our opinion, to the dibasic nature of sulphuric acid.

The structure of the film before and after diffusion is studied by small-angle X-ray diffraction. SAD patterns of polyamide feature a discrete reflection and a noticeably diffuse background (Figure 10). The reflection is generated by the areas with a regular alternation (with spacing d_M) of ordered or amorphous interlayers (lamellar structures or fibrils). The ordered areas in PA contain crystallites or paracrystallites. The background results from irregular alternation of the areas with different electron densities including microcavities. The intensities of the reflection I_r and the background I_b are presented in Table III as the ratios of the integral intensities measured for the films subjected to diffusion and the initial (dry) films. The spacings d_M are determined from the Bragg formula; the upper limit of the concentrations of crystallites and paracrystallites, by the method described in reference 22; the average radius of inhomogeneities R_d in the irregular part of the structure, by reference 23; the size distribution of inhomogeneities, by reference 24.

It follows from Figure 10 and Table III that the SAD patterns change even upon diffusion of water into the polymer, the intensities of both the reflection and background growing. It should be noted that the greater the intensity of X-ray scattering, the higher the heterogeneity of the matrix and the stronger the contrast of the electron densities of the constituent structural elements. It is known²⁵ that in the initial (dry) PA 6 there already exist voids with an average radius of about

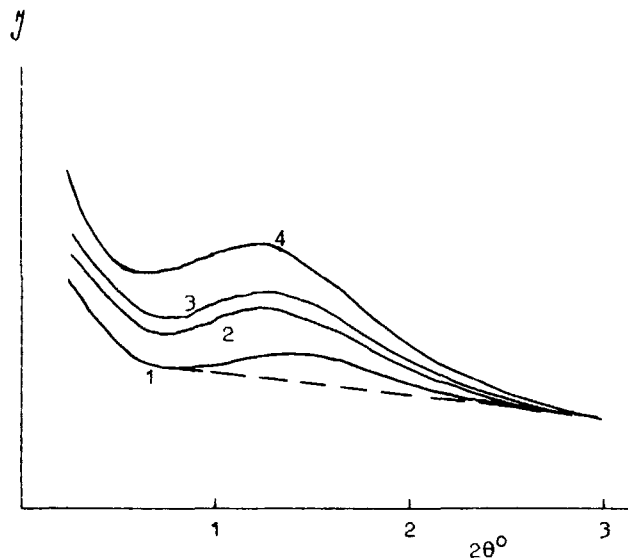


FIGURE 10 Small-angle X-ray diffraction patterns of PA 6 films: (1) initial dry film; (2) after holding in water for 24 h; (3) the same film after drying; (4) after holding in water for 24 h + 5 h in a solution of nitric acid + 5 days in water. The broken line refers to the background of the initial dry specimen.

10 Å. Calculations of the size distribution of inhomogeneities indicate the presence of a noticeable amount of these small inhomogeneities in PA 6 and PA 66. The total volume of the inhomogeneities, judging from the relative intensities I_r and I_b , grows under the action of water; however, the permeability of the films does not rise, which is possibly due to the closed character of the pores. The growth of the volume of the inhomogeneities under the action of water is irreversible: after drying, the characteristics of the structure of the specimens remain unchanged.

Subsequent treatment of polyamide films with a solution of nitric acid lowers the heterogeneity index of the lamellar fraction I_r ; together with this, the permeability of the films changed by 30–50%. Both facts point to the transformation of the previously closed pores into communicating voids accessible for diffusion of acids. Since the density of α crystallites is higher than that of paracrystallites γ^* (1.23 and 1.1 g/cm³, respectively), the repacking of the sections of macromolecules from γ^* paracrystallites into α crystallites, with the total volume of the specimen being unchanged, increases the free volume in the polymer. The areas that arise with lowered density facilitate the diffusion transport.

The development of the heterogeneity of the structure of polyamides under discussion is based on the repacking of macromolecules in the amorphous and paracrystalline areas and also on additional packing in the crystalline area which is possible on plasticization of polyamides with water, on the one hand, and on acid-induced rupture of hydrogen bonds fixing the structure at the boundary between the phases of different orderliness, on the other.

In conclusion it should be noted that the diffusion model proposed here makes it possible to explain the major principles governing the transport of mineral acids

in PA 6, to describe the kinetics of structural changes, and to calculate, using the model, the parameters characterizing the properties of the polymer/water system. The use of the main points of the model for arbitrary boundary conditions of interaction between the polyamide and the aggressive medium allows one to predict the performance characteristics of polymer systems in which the diffusion of a component is accompanied by redistribution of hydrogen bonds.

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