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Diffusion and Sorption of Aqueous Electrolyte Solutions in Polymers

G.E.Zaikov

The diffusion and solubility of electrolytes in polymers of different types (hydrophobic, hydrophilic, and moderately swelling) are examined. Diffusional transport in such systems is characterised by a number of features: dissociation, ion hydration, the formation of water clusters, and interaction with the functional groups of the polymer. The concentration dependence of the diffusion coefficients is analysed taking into account these effects and also the influence of the volume fraction of the polymer on the diffusion parameters. The mechanism of the distribution of the electrolyte in the hydrophobic and hydrophilic matrices is examined; it is shown that in the latter case account must be taken of the electrostatic factor, which influences the solubility of ions in polymers with ionogenic groups.
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I. INTRODUCTION

The investigations by Academician N.M.Emanuel' and his school on the degradation and stabilisation of polymers have led to the establishment of an independent and important field of chemical science dealing with such topics. It concerns the study of the structure and morphological changes in polymers as well as rational methods for controlling and regulating these changes.[1,2] When polymeric materials come into contact with liquid corrosive media, hydrolytic degradation takes place involving the diffusion of the components of the corrosive medium (acids, bases, salts, and water). In many cases of practical importance the rate of diffusional transport determines the limiting conditions under which polymers can be used. For example, the required properties of anticorrosion coatings in petroleum and gas mains include low diffusion coefficients in them of atmospheric and soil moisture as well as electrolytes; the polymer coating can then be used for a long time. On the other hand, self-degrading coatings of medicinal drugs or dialysis membranes should possess effective transport characteristics, which permit a productive and controllable liberation of medicinal drugs or separation of components.

The mechanism of diffusional transport in aqueous electrolyte solutions in a polymer is determined to a significant extent by the strength of the interaction between water molecules and macromolecules.[3] The subdivision of polymers into hydrophobic, hydrophilic, and moderately hydrophilic, proposed by Reitlinger,[4] therefore appears quite natural. Although the classification of hydrated polymer systems known at the present time as hydrophobic (in which the equilibrium water content under normal conditions and for 100% humidity is not more than 1%), hydrophilic (containing more than 10% water under the same conditions), and moderately hydrophilic (with an intermediate water content) simplifies the overall picture of the interaction of polymers with water, nevertheless it is also convenient from the practical point of view. In considering the diffusion of electrolytes, we shall adhere to this classification. We shall only note that the arbitrary nature of such subdivision arises from the dependence of the strength of the interaction of the macromolecules with water on temperature and from the variation of the degree of crystallinity of the polymer (recrystallisation, conversion into an amorphous form).[5]

The degree of hydrophilicity, i.e. the content of the water which has undergone equilibrium dissolution in the bulk of the polymer, can be estimated quantitatively with the aid of the solubility parameter δ ($J^{1/2}$ $m^{-3/2}$) [6] using the method of group contributions[7] and the Flory–Huggins theory of polymer solutions.[8]

Information about the overall content of water in the polymer is of limited value for measurements of the rate of diffusion, because the same amount of water can exist either in the bound state in the vicinity of polar groups of the macromolecules or can be distributed freely in the hydrophobic region. The mobilities of water molecules in the bound and free states are different.[9] The most reliable information about the transport mechanism is provided by the combined use of diffusion measurements and spectroscopic and relaxation methods. It is then possible to record not only the rate at which the electrolyte enters the polymer but also the structural changes accompanying diffusion.[10]

On the basis of extensive experimental data, one can assume that the first water molecules sorbed by the hydrophobic polymer are distributed between the units of the non-polar chain and that the energetic contribution of this process to the free energy of absorption is extremely low. A further increase in the moisture content in the system entails the preferential interaction between the water molecules and the consequent formation of clusters. This effect appreciably diminishes the mobility of water molecules, which is characterised by a decrease in the diffusion coefficients with increasing water concentration in the polymer.

Another situation arises in the diffusion of water in hydrophilic polymers. Here water molecules initially interact strongly with the highly polar groups of the polymer—the ionic and polar fragments are hydrated. The subsequent portions of water plasticise the polymer matrix, which leads, firstly, to an increase of the mobility of the segments (the polymer passes from the vitreous to the highly plastic state) and, secondly, to an increase in the fraction of "free" non-hydrating water in the polymer. Many hydrophilic polymers can undergo a transition under normal conditions into a viscous fluid state and they combine fully with water to form solutions provided that they are not cross-linked [poly(vinyl alcohol)(PVA), proteins]. Weakly cross-linked hydrophilic polymers can undergo limited swelling and their water content can reach several hundreds. The morphology

(porosity, crystallinity) of the hydrophilic polymers then changes significantly. A number of characteristic features of the diffusion of water in strongly swollen gels make it similar to the diffusion of water in solutions.

Moderately hydrophilic polymers combine with water to a limiting extent at room temperature even when they are in an amorphous state and are not cross-linked. They are also capable of the transition from the vitreous to the highly elastic state (for example, in the case of polyamides), of undergoing a change in the degree of crystallinity, and also of undergoing a change in the type of crystal lattice and pore deformation.[11] More refined effects, for example a transition from one crystalline modification to another (cellulose)[11] or the establishment of the liquid crystal state,[5] are also possible. When the transport of water is considered under conditions where the water content in polymers undergoing limited swelling is low, it is necessary to take into account the superposition of two transport mechanisms: one of them is analogous to diffusion in a hydrophilic polymer when the diffusing substance is in the vicinity of the polar group, while the other resembles diffusion in hydrophobic polymers when the water molecule overcomes hydrophobic regions whose dimensions significantly exceed the length of the diffusional jump. When the moisture content of the specimen is high, account must be taken of extensive hydrated regions where the macromolecules have been plasticised and the transport model should not differ greatly from the transport model in hydrophilic polymers.

II. DIFFUSION IN HYDROPHILIC POLYMERS

The multiplicity of phenomena accompanying the diffusion of electrolyte solutions in polymers can be characterised by the set of pair interactions presented in Table 1.[3] The predominance of a particular type of interaction depends on the nature of the polymer. For example, the diffusion in hydrophobic polyolefins and polysiloxanes is complicated by interactions of the water–water (cluster formation) and water–electrolyte type,[12] while in polar polymers the interaction of the polymer–electrolyte type becomes dominant.[13]

Electrolytes alter the physical structure of the polymer either by direct interaction with various polar and ionised groups or indirectly as a result of the influence of the ions on the structure and activity of the solvent. The direct interaction of ions with macromolecules can be both non-specific, i.e. can be determined by long-range Coulombic forces, and specific, being determined by the specific influence which the electrolyte exerts on the conformation of the macromolecules, for example, in its competition with water for the formation of hydrogen bonds with the functional groups of the polymer (guanidinium salts, hydrochloric and hydrofluoric acids) or in the course of the redistribution of hydrophobic contacts (tetra-alkylammonium ions) in the polymer.[14]

1. Relation between the Diffusion Coefficients and the Volume Content of the Polymer

It is useful to begin the examination of the diffusion of electrolytes in polymers in terms of the somewhat simplified but frequently employed Mecke-Meares and Yasuda theories (see, for example, Moiseev and Zaikov[15] p.119). The essential features of these theories consist in the attempt to relate the diffusional parameters of the solutes (the diffusion coefficient D and the permeability P) in hydrophobic polymers containing different amounts of water to the diffusion coefficient of the electrolyte in the pure solvent (D^0). On the basis of the above theories, it becomes possible to predict the diffusion coefficients of the electrolyte in the polymer D knowing only D^0 (tabulated data) and the volume concentration of water in the polymer ϕ_w (experimental data). Both theories treat the electrolytes as an individual substance; the effects of the ion–ion interaction, the deviations from ideality, and the possibility of partial dissociation are neglected.

Table 1. The types of interactions in electrolyte–water–polymer systems.[13]

Type of interaction	Nature of interaction	Manifestation at physicochemical level
Polymer-polymer	Electrical, polar, and dispersion interactions	Wide variety of ordered crystalline and supermolecular structures, the presence of three main physical states of the polymers (vitreous, highly elastic, and viscofluid)
Electrolyte-electrolyte	Electrical forces (ion-ion); ion-dipole interactions (for incompletely dissociated electrolyte molecules); hydrophobic interactions (for large organic ions)	The operation of Coulomb's law, the existence of an ionic atmosphere, dissociation, complex formation, etc.
Water-water	Dipole-dipole interactions	The existence of hydrogen bonds, the formation of ordered structures (clusters), cluster water-monomeric (free) water equilibrium
Electrolyte-water	Ion-dipole interactions	Hydration, formation of crystalline hydrates
Water-polymer	Polar and hydrophobic interactions	The hydration of polymer groups and segments, plasticisation, antiplasticisation, conformational transitions, crystallisation, transformations of crystal structures, conversion into an amorphous form, degradation, etc.
Electrolyte-polymer	Electrical and polar interactions, hydrophobic interactions (for large organic ions)	Conformational changes in macromolecules, change in crystal structure, complex formation, structure formation (by polyvalent ions), plasticisation

The Mecke-Meares theory of steric hindrance explains the decrease of the self-diffusion coefficients of electrolytes in hydrophilic polymers compared with aqueous solutions by the increase of the diffusional path, because the ions have to move round the macromolecules. In the absence of interaction between the functional polar groups of the polymer and the electrolyte, the polymer hindrance effect is taken into account by the factor

$$(1-\varphi_p)^2/(1+\varphi_p)^2,$$

where ϕ_p is the volume fraction of the polymer.

In contrast to the previous theory, Yasuda's theory uses the concept of the free volume instead of the mechanistic ideas about the polymer as a medium interfering with the movement of ions.[16] The hydrated polymer is regarded as a quasi-homogeneous matrix in which segmental movement of the macromolecules and the presence of the solvent result in the existence of an additive free volume

$$f_v = f_v^w \varphi_w + f_v^p \varphi_p, \qquad (1)$$

where ϕ_w and ϕ_p are the volume fractions and f_v^w and f_v^p are the free volumes of water and the polymer respectively. In formulating the expression for the diffusion coefficient of the electrolyte as a function of ϕ_w, the following assumptions

are made: (1) the effective free volume, in which the solute (electrolyte) is accommodated, corresponds to the free volume of water in the polymer, i.e. account is taken only of the first term of Eqn.(1); (2) the size of the fluctuating cavities, which determine the free volume, corresponds to the size of the diffusing species; (3) there is virtually no interaction between the polymer and the solute molecules.

The probability of the formation of a cavity whose dimensions correspond to the cross-sectional area of the diffusing species (S_S) is defined as $\exp(-BS_S/f_V)$, where B is a constant, for small electrolyte species. In this case the diffusion coefficient of the electrolyte in the polymer, where the volume fraction of water is ϕ_w, is defined by the equation

$$D = D^0 e^{-k_f(1-\Phi_w)\Phi_w^{-1}}, \qquad (2)$$

where $k_f = BS_S/f_V^w$.

It follows from Eqn.(2) that the diffusion coefficient D increases with increasing concentration of water in a hydrophobic polymer, approaching in the limit the diffusion coefficient of the electrolyte in pure water, which has been confirmed in a series of experiments. With decrease of the water content in the specimen, the diffusion coefficient of the electrolyte also falls. The shielding effect of water becomes weaker, so that the possibility of the direct interaction of the electrolyte ions with the macromolecules increases and Eqn.(2) ceases to hold for sufficiently low values of ϕ_w. It is therefore important to emphasise that, from the standpoint of the model considered, the polymer influences the diffusion of the electrolyte only indirectly by reducing the fraction of the free volume of water in the system.

Two important corollaries follow from Eqn.(2). Firstly, the dependence of $\lg D$ on ϕ_w^{-1} is more pronounced the greater the cross-sectional area of the diffusing species. Secondly, for a series of species of different cross-section and within a specific range of values of ϕ_w, the quantity $\lg(D/D^0)$ should decrease linearly with increasing S_S and the higher the water content in the polymer the more marked should be this dependence. To illustrate this conclusion, we shall resort to the results of a study[17] in which the above dependence was observed for a series of organic compounds diffusing in poly(hydroxyethyl methacrylate) hydrogels (Fig.1). The introduction of a cross-linking agent diminishes the water content in the polymer and, as follows from Eqn.(2), leads to a sharper decrease of the diffusion coefficient with increasing r^2, where r is the radius of the diffusing molecule.

Yasuda's model does not take into account the specific features of the electrolyte as a substance capable of dissociating into ions and it is therefore applicable mainly to natural solutes and does not describe the diffusion in polymers containing charged ionogenic groups (ion-exchange resins, polyelectrolytes).[18]

2. The Influence of the Ionogenic Groups of the Polymer on the Diffusion of Electrolytes

The question of the influence of the ionogenic groups of the polymer is important for understanding the mechanism of the processes involving the dyeing and hydrolytic degradation of synthetic and natural fibres, mainly polyamides; the influence of the charged groups on the transport of electrolytes in these polymers, which belong to an intermediate class, will be examined in greater detail in the next Section.

Nikolaev and co-workers[19,20] have made a considerable contribution to the development of ideas about the mechanism of the diffusion of electrolytes in ion-exchange resins. Ion-exchange resins as a rule contain large amounts of water and can be formally classified as hydrophilic polymers. In order to explain the diffusion in hydrophilic polymers containing ion-exchange groups, a loose quasi-crystal model has been proposed.[19] It is based on the following postulates: (1) owing to thermal movement, the counterions can move away from the functional group of the polymer and can give rise to defects resembling those in ionic crystals (vacancies and incorporated ions); (2) migration in the membrane takes place in two stages: during a period τ_0, the counterion is in a potential well, whose existence is due to the presence of the functional group, and oscillates about the equilibrium position. After that, during a period τ_1, it diffuses in a medium analogous to an electrolyte solution until it reaches the next functional group; (3) the functional groups are uniformly distributed in the polymer and in the swollen state the system is quasi-homogeneous.[20]

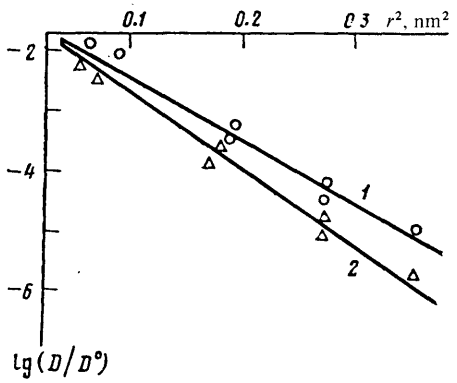


Figure 1. The influence of the size of the diffusing species on the diffusion coefficients in poly(hydroxyethyl methacrylate): 1) $\phi_w = 0.42$; 2) $\phi_w = 0.37$.[17]

The diffusion coefficient of the counterion in the polymer is determined by the two characteristic times τ_0 and τ_1:

$$D_i = \lambda^2/[6(\tau_0+\tau_1)]^{-1}, \qquad (3)$$

where λ is the average distance between the nearest ionogenic groups, which is calculated on the basis of a scheme assuming the closest packing with the aid of the formula $6.6 \times 10^{-9} C_p^{-1/3}$ (C_p is the capacity of the swollen material, equiv.m^3). After the introduction of the tortuosity coefficient of the diffusion path (r_0) the final expression for the effective diffusion coefficient of an ion in the polymer is

$$D_i = D_i^0 r_0/[(\tau_0/\tau_1)+1], \qquad (4)$$

where D_i^0 is the diffusion coefficient of the ion in solution.

Experimental measurements of the rate of diffusion in ion-exchange materials of different chemical nature indicate the possibility of the variation of D_i by 5–7 orders of magnitude, while the diffusion coefficients of ions in aqueous solutions vary only within the limits of one order of magnitude. Analysis of experimental results enabled the author to conclude that the main parameter determining the rate of diffusion in polymers is the residence time of the counterion in the vicinity of a given functional group. The stronger the bond between the counterion and the functional group, the longer the time τ_0 and hence the lower the diffusion coefficient.

A decrease in the water content of ion-exchange membranes, for example, as a result of the increase of the degree of cross-linking, strengthens the bond between the counterion and the functional group as a consequence of the diminution of the degree of their hydration. The decrease in the dielectric constant in the system when electrolytes diffuse from non-aqueous solvents also has a negative influence on the ionic mobility. For example, comparison of the diffusion coefficients of the Na^+ and Cs^+ ions in a Nafion membrane from aqueous solutions and acetonitrile ($\varepsilon = 37.5$) solutions showed that the diffusion parameters diminish in the less polar medium approximately by a factor of 120 for Na^+ and 550 for Cs^+.[21]

The presence of dissociating groups in the polymer complicates the electrolyte diffusion process as a result of the occurrence of ion-exchange reactions. The appearance of maxima on the kinetic curves for the sorption of electrolytes by polymers, which are absent in experiments with pure water, characterises the different capacities of the dissociating SO_3H and $SO_3^-M^+$ groups for the sorption of water (M^+ is a metal cation which can give rise to a neutral form).[22]

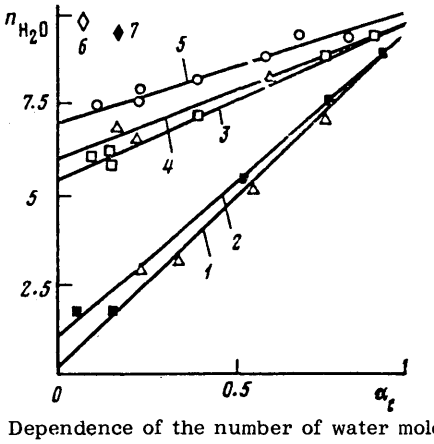


Figure 2. Dependence of the number of water molecules sorbed on the counterions of a "Nafion" membrane on the degree of substitution of the proton by the cation of the SO_3H group: 1) K^+; 2) Cs^+; 3) Ba^{2+}; 4) Sr^{2+}; 5) Ca^{2+}; 6) Al^{3+}; 7) Fe^{3+}.[22]

During the diffusion of a solution of alkali into a polymer specimen containing strongly acid groups, the latter are neutralised. At each instant, the following equation holds:

$$n_w = n_h(1-\alpha_c) + \alpha_c n_k = (n_h - n_k)(1-\alpha_c) + n_k, \qquad (5)$$

where n_h, n_k, and n_w are the numbers of moles of water sorbed by one mole of the acid and the neutral form of the sulpho-groups and the number of moles of water sorbed per mole of the counterion respectively and α_c is the degree of substitution of the proton in the SO_3H group by the cation.

In conformity with this equation, there is a linear relation between n_w for SO_3H and $1 - \alpha_c$. Fig.2 shows that the total amount of sorbed water per sulpho-group in the neutral form increases with increasing charge of the counterion in the sequence $K^+ < Cs^+ < Ba^{2+} < Sr^{2+} < Ca^{2+} < Fe^{3+} \cong Al^{3+}$, which can be explained by the polarising influence of the ion on the nearest water molecules. The diffusion kinetics of ion exchange are described in greater detail in a monograph.[23]

3. The Influence of the Chemical Structure of the Polymer on Diffusion

The term "chemical structure of the polymer" is understood as the chemical composition, the sequence of elementary units, and the degree of branching of the polymer chain. The principal characteristics of the chemical structure are the polarity of the macromolecule, steric factors (i.e. the stereoregularity of the macromolecule), and the ability of the molecules to form hydrogen, polar, and van der Waals linkages. There are important reasons to believe that the chemical structure determines the possibility of the existence of a structural hierarchy of polymers: the presence of α- and β-helices, crystallinity, supermolecular formations, porosity, etc. The possibility of obtaining a polymeric particle (membrane, coating, etc.) with the necessary degree of crystallinity or porosity depends on specific conditions in the preparation and previous history of the specimen: the choice of the solvent, the rate of its evaporation, the existence of temperature gradients, the character of the support, the storage conditions, and a number of others.[24,25]

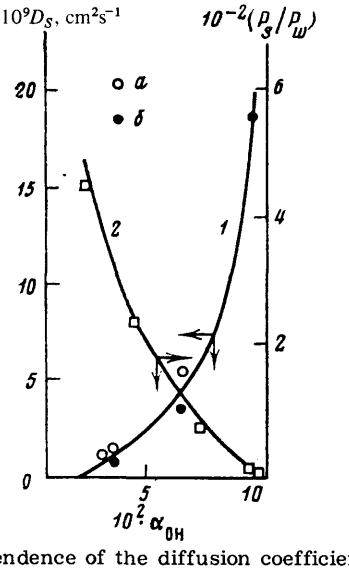


Figure 3. Dependence of the diffusion coefficients of NaCl (curve *1*) and of the relative permeability to the salt and water (curve *2*) on the weight fraction of the hydroxy-groups in cellulose acetate: *a*) stationary measurements; *b*) measurements of the delay time.[3]

As in the transport of water molecules, the permeability to and diffusion of electrolytes are regulated by the ratio of the hydrophilic and hydrophobic units of the macromolecules. Fig.3 presents the diffusion coefficients and the relative permeabilities for a salt and water (P_{NaCl}/P_W) in cellulose acetate films. Evidently, with increase of the weight fraction of hydroxy-groups, i.e. with decrease of the degree of acetylation, a sharp increase of the rate of diffusion of sodium chloride is observed. The principal cause of the increase of P_{NaCl} is the increased water content in the more hydrophilic matrix, which entails the plasticisation of the macromolecules and hence an increase in the free volume in the system.

The accompanying decrease of the relative permeability shows that, despite the overall tendency towards an increase of P_{NaCl}, the value of P_w under the conditions of an applied hydrostatic pressure increases faster, since the mechanism of water transport in strongly swelling membranes changes from diffusional to convective.[26]

A large difference between the mechanisms of the permeability of cellulose and nitrocellulose membranes has been demonstrated.[27] Since the conformations of the molecules of the modified and unmodified celluloses are virtually identical according to infrared spectrscopic data, the above differences can be caused only by the interaction of the OH and NO_2 groups with the solvent and solute and also by some increase in the size of the cavities accompanying the replacement of the nitro-groups in nitrocellulose by hydroxy-groups.

Interesting studies of the influence of the ratio of hydrophilic and hydrophobic units in the macromolecule have been made using membranes based on poly(ethylene terephthalate)-poly(hydroxyethylene glycol) (hydrophilic component) block-copolymers. Membranes of this type are used in medicine for the purification of blood plasma by removing low-molecular-weight impurities, salts, and urea. The linear dependence of the purification half-life on the content of the hydrophilic component in the matrix indicates the need to take into account the ratio of the hydrophilic and hydrophobic groups in the polymer in the solution of practically important problems in membrane separation. An increase of the content of poly(hydroxyethylene glycol) in the copolymer increases the degree of its swelling, which impairs, in its turn, the selectivity and mechanical properties of the film used for dialysis. In constructing separators, oxygenators, dialysis apparatus, etc., it is therefore necessary to select optimum conditions which ensure a high productivity of the membrane and reliable operating qualities of the given article. The hydrophobic blocks play an important role in the fulfillment of the latter requirement. By crystallising and forming domains, they protect the hydrophilic matrix from extensive swelling or dissolution, forming, as it were, effective cross-links.[25]

Membranes based on ethylene–potassium acrylate (25%) copolymers are used in silver-zinc accumulators. When styrene is grafted to the copolymer, the resistance of the polymer matrix to oxidative degradation in the electrolyte improves. It has been shown by an isotopic method that the permeability of membranes to OH^- ions passes through a maximum corresponding to a grafted styrene content of 2.5%, whereas a further increase of the hydrophobic component entails a decrease of P_{OH^-}, as was to be expected. The permeability to Ag^+ ions under the same conditions diminishes monotonically and, in the presence of 16.5% of styrene, the membrane becomes impermeable to Ag^+ ions.[28] These data as well as the results of a number of other studies show that specific conclusions about the influence of the hydrophilic-hydrophobic balance must be made to take into account the specific nature of the diffusing ion. In the example described above the hydroxide ion, as well as the H^+ ion, is characterised by an anomalous diffusional behaviour not only in solution but apparently also in many polymer systems capable of forming hydrogen bonds.

4. The State of the Electrolyte in the Polymer

(a) Ion hydration. The theory of the diffusion of electrolytes in polymers deals with hydrated species and ions as independent kinetic units and does not take into account quantitatively the exchange between the free water and the water of hydration, i.e. the dynamic character of hydration. The polymer matrix is regarded as an inert medium, usually quasi-homogeneous, in which there is sufficient water to ensure, firstly, the hydrolytic dissociation of the electrolyte and, secondly, that the ionic and functional groups of the macromolecules are in a hydrated state.

The commonest evidence for the presence of a hydration shell around the ions diffusing in a hydrophilic polymer is the observation that the sequence in which their diffusion coefficients vary is the same as for their diffusion coefficients in solution. The decrease of the diffusion coefficients of singly charged and multicharged ions in hydrophilic and weakly cross-linked polymer membranes corresponds to an increase of the radius of the hydrated ion and not to its crystallographic radius:[3]

$$D(Cs^+) > D(Rb^+) > D(K^+) > D(Na^+) > D(Li^+);$$
$$D(Na^+) > D(Ca^{2+}) > D(Y^{3+}) > D(Th^{4+})$$

However, for a low water content in moderately hydrophilic polymers, the sequence of the diffusion parameters can be inverted. For example, the decrease in the diffusion coefficients in polyamides (nylon-6) corresponds to the increase of the crystallographic radii of the singly charged cations Na^+, Rb^+, and Cs^+.[29] In exactly the same way, the activation energy for conduction by salts in nylon-6,6 and nylon-6 increased with increase in the crystallographic radius (Table 2). This result made it possible to conclude that there is no hydration, or the latter is extremely limited, in polyamides containing not more than 8% of water.[29]

Table 2. The activation energies for electrical conduction by various salts in nylons (electrolye concentration 0.1 M).

Polymer	Activation energy, kJ mol^{-1}			
	LiCl	NaCl	KCl	RbCl
Nylon 6	44.0	54.4	59.2	65.2
Nylon 6,6	49.4	54.5	—	57.0

With a high moisture content ($\phi_w = 0.7–0.9$) in the same polymer, namely poly(vinyl alcohol), the mutual diffusion coefficients, determined interferometrically, increase in the sequence

$$D(K^+) > D(H_2O) > D(Na^+) > D(Mg^{2+}),$$

i.e. the same sequence as that corresponding to the increase of the radius of the hydrated ion (0.27, 0.30, 0.35, and 0.42 nm respectively), while in the presence of a low moisture content ($\phi_w = 0.1–0.2$) the same diffusion parameters increase in conformity with the increase in the crystallographic radius[30] in the sequence

$$D(Mg^{2+}) > D(Na^+) > D(H_2O) > D(K^+).$$

Information about the state of the ion in a polymer matrix and about its diffusional mobility can be obtained directly by EPR spectroscopy. However, we may note that this method is applicable only to a limited number of paramagnetic ions such as Cu^{2+}, Mn^{2+}, Fe^{2+}, VO^{2+}, etc. Nevertheless, the extensive possibilities and high sensitivity of EPR spectroscopy made it one of the most promising methods for the investigation of the state of an electrolyte in a polymer, which has come to be widely used in physicochemical and biological research.[31,32]

The degree of interaction of water molecules with ions in a polymer matrix can be estimated quantitatively by analysing the dependence of the chemical shift of the proton signal, recorded by NMR, on temperature, moisture content, the nature of the ion, and certain other parameters. The position of the ^1H NMR signal of the water sorbed by the polymer depends on the capacity of the diffusing ion for hydration. The greater the polarising power of the cations, the greater the downfield shift of the signal. If electrostatic forces are mainly responsible for the polarisation of water molecules near the ion, the chemical shift should be proportional to the ratio of the ionic charge to the square of the crystallographic radius of the ion, i.e. the distance from the centre of the ion to the nearest molecule (z_i/r^2). Such a relation has been observed for a series of alkali and alkaline earth metal cations in the KU-2 cation-exchange resin.[33] The Rb^+ and Cs^+ ions, which have such large radii that electrostatic forces become weaker than those governing the interaction of the water molecules with one another and with the functional groups of the polymer, are an exception. An analogous linear relation has been observed also for anions.

In the course of the desorption of water from the polymer, the hydration shell of the ion is disrupted. The dielectric constant of the system falls and the dissociating cation–anion pair acts on water as a dipole and not as individual point charges. The position of the signal of the water protons undergoes a sharp upfield shift in this case. At a water concentration in the polymer approximately equal to two water molecules per ion and less, the NMR method does not make it possible to estimate the chemical shift as a consequence of the broadening of the resonance lines in the proton, which restricts the application of the method to moderately and weakly swelling polymers.[33]

(b) Dissociation of the electrolyte. The state of the electrolyte in a polymer is determined by the ratio of its ionised and unionised forms, i.e. by the degree of its ionisation. Other conditions being equal, the degree of ionisation depends on the electrolyte concentration. It is therefore useful to characterise the ionisation of an acid or base by the thermodynamic dissociation constant, which determines the strength of the given electrolyte in the diffusion medium and does not vary with concentration.

Depending on whether the electrolyte exists in the polymer in a dissociated form or as neutral molecules, the mechanism of the diffusional transport varies. For example, in the case of an acid, dissociation leads to the appearance in the system of the most mobile form of the protons. In addition, many degradative processes occurring in the polymer via an acid or base-catalysed mechanism are also determined by the concentration of hydroxide and hydronium ions.[15] Information about the state of the electrolyte in the polymer is therefore extremely important not only for the understanding of the diffusion mechanism but also for the prediction of changes in the system as a whole (decrease of the molecular weight and viscosity, a change in the ratio of the crystalline and amorphous phases, etc.).

The methods are known for the determination of the ionisation constant of an electrolyte in hydrophilic polymers: the ion-exchange method,[34] the spectrophotometric (indicator) method, and the conductimetric method.[35]

Table 3 presents the pK for certain electrolytes in hydrophilic polymers saturated with water. It is noteworthy that the dissociation constants of electrolytes hardly differ from the corresponding parameters in pure water in all the cases considered. This effect can apparently be accounted for by the shielding influence of water, which prevents the interaction of the electrolyte with the polymer molecule.[35]

5. Dependence of Diffusion Coefficients on the Electrolyte Concentration

The concentration dependence of diffusion coefficients characterises the features of electrolyte transport in hydrophilic polymers. In the general case its manifestation is due to the following factors: the differences between the mobilities of the dissociated and undissociated forms of the electrolyte; the non-ideal thermodynamic behaviour of the polymer–electrolyte solution system; the interaction of the ions with the functional groups of the polymer; the change in the structure of the polymer as a result of swelling.[36]

Table 3. The ionisation constants of electrolytes in hydrophilic polymers (pK) and in water (pK_w).

Electrolyte	Polymer matrix	c_w, wt.%	pK_w	pK	Method	Refs.
Glycine	KU-2 cation exchanger	60	2.34	2.49	1	[34]
Lysine	ditto	60	2.18	2.71	1	[34]
Lysine	»	60	8.95	9.06	1	[34]
Glutamic acid	»	60	2.18	2.12	1	[34]
α-Alanine	»	60	2.34	2.45	1	[34]
μ-Nitroaniline	Dowex 50 x 1	60	2.51	2.60	2	[3]
μ-Nitroaniline	PVA	78	2.51	2.59	2	[35]
H_3PO_4	»	78	2.12	2.14	3	[35]
H_3PO_4	»	38	2.12	2.15	3	[35]

Notation. Methods: 1) ion exchange; 2) spectrophotometric; 3) conductimetric; c_w = water content in the polymer.

(a) The influence of dissociation on the diffusional transport of the electrolyte. In a hydrophilic polymer the electrolyte can exist in partly or fully dissociated states. If the diffusing species formed as a result of the dissociation of the electrolyte have different mobilities, then the overall mobility of the electrolyte should be determined by the degree of its dissociation α_c:

$$D=\alpha_c D_s+(1-\alpha_c)D^u, \tag{6}$$

where

$$D_s=\frac{2D_C D_A\,(z_C-z_A)}{z_C D_C-z_A D_A}, \tag{7}$$

where D_A and D_C are the diffusion coefficients, z_A and z_C are the charges of the anion and cation respectively, and D^u is the diffusion coefficient of the undissociated species.

In order to account for the concentration dependence of the diffusion coefficients in the polymer, we shall formulate Fick's equation as follows:[37]

$$J_{H_mA}=-\sum_{m=1}^{m}[D_{H^+(A^{m-})}\nabla c_{H^+(A^{m-})}-D^u_{H_mA}\nabla c^u_{H_mA}], \tag{8}$$

where $D_{H^+(A^{m-})}$ and $D^u_{H_mA}$ are the diffusion coefficients of the dissociated and undissociated forms of the acid H_mA respectively, $c_{H^+(A^{m-})}$ and $c^u_{H_mA}$ are the concentrations of the corresponding forms, and J_{H_mA} is the flux of the diffusing acid. In all subsequent examples, the diffusion coefficients will be assumed to be constant.

In solutions with centimolar concentrations, hydrochloric acid is almost fully dissociated and Eqn.(8) becomes

$$J_{HCl}=-D_{H^+(Cl^-)}\nabla c_{H^+}. \tag{9}$$

Here

$$D_{H^+(Cl^-)}=2\cdot D_{H^+}D_{Cl^-}/(D_{H^+}+D_{Cl^-}) \quad \text{and} \quad c_{H^+}=c_{Cl^-}=c_{HCl}.$$

Eqn.(9) demonstrates the constancy of the diffusion coefficients of any strong acid in strongly swelling hydrophilic polymers. The absence of a concentration dependence of $D_{H^+(A^-)}$ has been observed experimentally for hydrochloric and trichloracetic acids.[3]

In the experimental concentration range, the strong dibasic acid H_2SO_4 undergoes appreciable dissociation of the second proton and the hydrogen ions diffusing in a neutral polymer matrix are surrounded by SO_4^{2-} and HSO_4^- ions. In this case Eqn.(8) makes it possible to obtain an expression for the effective diffusion coefficient:

$$D_{eff}=D_{HSO_4^-}\left[1+\frac{(\beta-1)}{(1+c_{H^+}/2K_2)^2}\right], \qquad (10)$$

where $K_2 = 1.25 \times 10^{-2}$ is the second dissociation constant of sulphuric acid and $\beta = D_{SO_4^{2-}}/D_{HSO_4^-}$ is the ratio of the diffusion coefficients of the individual ions.[37]

Analysis of Eqn.(10) shows that, if $\beta = 1$, i.e. when $D_{SO_4^{2-}} = D_{HSO_4^-}$, a single diffusion coefficient would be sufficient for the description of diffusional transport. At low acid concentrations $c_{H^+} \ll K_2/2$ and $D_{eff} = D_{HSO_4^-}\beta = D_{SO_4^{2-}}$. Indeed, the fraction of SO_4^{2-} ions in the bulk phase increases with increasing dilution of H_2SO_4 and in the limit transport involves only bivalent ions. On the other hand, at high acid concentrations, where $c_{H^+} \gg K_2/2$, the SO_4^{2-} ions are almost absent. Graphical solution of Eqn.(10) in terms of the variables D_{eff} and $(1 + c_{H^+}/2K_2)^{-2}$ made it possible to determine β, $D_{HSO_4^-}$, and $D_{SO_4^{2-}}$, which are 0.15, 5.9×10^{-10} $m^2\ s^{-1}$, and 0.9×10^{-10} $m^2\ s^{-1}$ respectively.[37] The lower diffusion coefficient of the bivalent SO_4^{2-} ion compared with that of the HSO_4^- ion indicates an increase of the diffusional resistance of the medium as a consequence of the increased hydration of multicharged ions and also stronger electrostatic and specific interactions in the polymer matrix.

In the case of phosphoric acid, which is weaker than the acids examined above, Eqn.(8) assumes the following form:

$$D_{eff}=D_{H^+(H_2PO_4^-)}\left[1+\frac{2\beta_1}{K_1}c_{H^+}\right], \qquad (11)$$

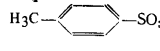
where $K_1 = 7.51 \times 10^{-3}$ is the first dissociation constant of phosphoric acid and $\beta_1 = D_{H^+(H_2PO_4^-)}/D_u$. Eqn.(11) predicts a linear increase of the diffusion coefficients with increasing concentration, which has indeed been observed in the transport of H_3PO_4 in water-saturated PVA films.

A linear increase of D_{eff} with increasing concentration c_{H^+} is observed for H_3PO_4 in the range of moderate concentrations, but in highly dilute solutions ($c_{H^+} = 2.5 \times 10^{-3}$ equiv. dm^3) there is an appreciable deviation from linearity. This effect has been explained[37] by the specific binding of the diffusing acid species in the polymer matrix.

For the almost fully dissociated acids HCl and CCl_3COOH as well as for the undissociated acetic acid CH_3COOH, there is no concentration dependence of the diffusion coefficients over the entire experimental concentration range.

In conclusion of this Section, we present in Table 4 the diffusion parameters of a series of acids of different types, determined in PVA films containing 75–78% of water. For comparison, the corresponding diffusion coefficients of the same acids in pure water are also quoted. Comparison of the diffusion parameters of different organic acids indicates the important role of the size of the diffusing species. The molecular diameter increases on passing from acetic to toluene-*p*-sulphonic acid, while the diffusion coefficients diminish in the same sequence.

Table 4. Diffusion parameters of acids in PVA films containing 75–78% of water ($\bar{D}$) and in pure water (D^0).[3]

Acid	$10^{10}\bar{D}$, m^2s^{-1}	$10^{10}D^0$, m^2s^{-1}	$\bar{D}/D^0$
$H^+(Cl^-)$	14.0	30.0	0.47
HSO_4^-	5.9	12.3	0.48
CH_3COOH	4.1	12.0	0.34
$H^+(ClCH_2COO^-)$	3.7	11.1	0.33
$H^+(Cl_3CCOO^-)$	3.2	10.4	0.31
SO_4^{2-}	0.90	2.2	0.41
	0.75	—	—

III. DIFFUSION IN MODERATELY HYDROPHILIC POLYMERS

Moderately hydrophilic polymers contain a limited number of polar groups. Typical examples of polymers of this class are the polyamides, the amount of water which they absorb under normal conditions being 2–10%. Numerous studies of the sorption and diffusion of electrolytes have been carried out on polyamide specimens, which reflects the great interest of investigators in the problem of dyeing by acid and basic dyes.[38] Polyamide membranes are widely used in dialysis and reverse osmotic systems.[39] The purely technological problems involving the search for the optimum dyeing, purification, or separation conditions give rise to a problem of great theoretical importance, namely that of the study of the mechanism of the interaction of low-molecular-weight components in a polymer matrix.

The characteristic features of the diffusion of charged species into polar polymers which distinguish the latter from non-polar polymers are related to the strong interaction of such species with the functional groups characteristic of, for example, the polyamides ($-NH_2$, $-COOH$, $-CONH-$). Such interaction may entail the complete loss of mobility by some of the diffusing ions or an exchange interaction with the functional group R in accordance with the scheme

$$R + E \underset{}{\overset{K}{\rightleftharpoons}} RE.$$

When the number of binding groups exceeds the number of electrolyte molecules (E), for example those of HCl in polyamide 6, the diffusion is retarded in accordance with the equations

$$\frac{\partial c}{\partial t}=D_{eff}\frac{\partial^2 c}{\partial x^2}; \quad D_{eff}=D/(1+K[R]_0), \qquad (12)$$

where D is the true diffusion coefficient, $[R_0]$ the concentration of the reacting groups in the polymer, K the exchange equilibrium constant, and x the diffusion coordinate.

For a correct interpretation of the results of diffusion experiments, it is essential to know the composition and state of the electrolyte and the nature and distribution of the polar groups of the polymer.

1. The Influence of the Ionogenic Groups of the Polymer on the Concentration Dependence of the Diffusion Coefficients

In the initial state the polyamide macromolecules contain unequal numbers of terminal amino-groups B_0 and carboxy-groups A_0. Some of the amino- and carboxy-groups are linked to one another in a zwitter-ionic form. The sorption of acid under conditions where $B_0 > A_0$ therefore includes three consecutive stages:

$$\begin{gathered} R{-}NH_2 + HCl \xrightarrow{(a)} R{-}NH_3Cl, \\ R{-}NH_3^+{-}R{-}COO^- + HCl \xrightarrow{(b)} R{-}COOH + R{-}NH_3Cl, \\ R{-}CONH{-}R + HCl \xrightarrow{(c)} R{-}NH_2^+COO{-}R(Cl^-), \end{gathered} \qquad (13)$$

If $A_0 > B_0$ in the polymer, then only reactions (b) and (c) take place.

Despite a number of limitations, the proposed scheme (13) can explain certain experimental facts (see Zaikov et al.,[3] p.123). The role of a neutral electrolyte, for example KCl, present in the polymer has been examined by Crespo.[40]

As a result of the interaction of the diffusing ions with the ionogenic and polar groups of the polymer, a dependence of the mobility of the ions on the degree of binding of these groups (the degree of filling of the adsorption sites θ_f) is observed in the initial stages of the sorption process. With increased concentration of the acid in the polymer, the functional groups are deactivated in accordance with scheme (13) and their electrostatic and chemical influences on the diffusing ions and molecules diminish. When the acid concentration has passed through a critical region where the condition $c_{A_0} = c_{HA}$ holds, the diffusion coefficient of the electrolyte increases sharply. For example, the self-diffusion coefficient of sulphuric acid in the amine region of polyamide 6, measured by the radioactive isotope method, is described by the analytical expression[41]

$$D^*_{H_2SO_4} = \frac{K}{2K_2}\frac{\theta_f}{(1-\theta_f)}D^*_{HSO_4^-} + \left[1 - \frac{K}{2K_2}\left(\frac{\theta_f}{1-\theta_f}\right)\right]D^*_{SO_4^{2-}}, \qquad (14)$$

where θ_f is the degree of occupation of the terminal amino-groups and K/K_2 is the ratio of the equilibrium constant of reaction (a) in scheme (13) to the second dissociation constant of H_2SO_4. The agreement between the experimental and theoretical results can be seen from Fig.4. An analogous sharp increase in the effective diffusion coefficients in polyamides is observed predominantly for cations (protons) in the HBr–polyamide-6,6 and sulphuric acid–keratin systems.[3]

In diffusion systems where there is an equilibrium between the freely diffusing ions and ions bound to the functional groups of the polymer, the activity coefficient is determined by the ratio $\gamma = D_{eff}/D_i$, where D_i is the diffusion coefficient of the free ion, which is independent of the concentration.

As regards inorganic acid anions, the concentration dependence of their diffusion coefficients is less marked. For example, the self-diffusion coefficient of the Br^- ions in the amine region of polyamide 6,6 is almost independent of the acid concentration and increases slightly in the amine region (from 6×10^{-15} to 10^{-14} m^2 s^{-1}). The diffusion coefficient of the Cl^- ion in polyamide 6 at 70 °C also depends only slightly on the concentration over a wide range of degrees of saturation of the adsorption sites:[3]

θ_f	0.19	0.40	0.75	0.82
$10^{11}D_{Cl^-}$, m^2s^{-1}	0.40	0.45	0.49	0.52

The coefficients $D_{SO_4^{2-}}$ and $D_{HSO_4^-}$ depend more markedly on the concentration but even their concentration dependence is less pronounced than that of D_{H^+}.

The complex dependence of the diffusion coefficients of the anions of organic dyes on concentration reflects the interaction of the moving anions not only with the polymer matrix but also with one another.

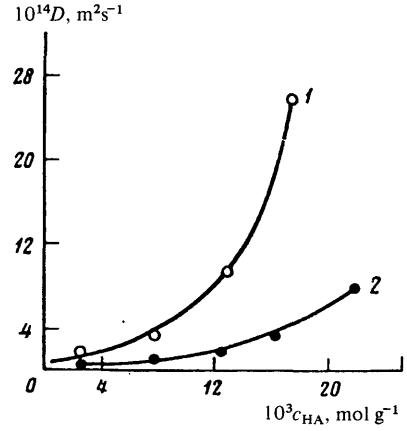


Figure 4. Dependence of the diffusion coefficients of sulphuric acid in polyamide 6,6 at 25 °C on its concentration;[41] 1) $D(H_2SO_4)$; 2) $D(SO_4^{2-})$; circles—experiment; continuous curves—calculated data.

The diffusion of organic acids has been studied in less detail than that of inorganic acids, but the relations obtained suggest that the mechanism of their sorption in the amine region is the same as that of inorganic acids. Table 5 presents the diffusion and thermodynamic parameters for the sorption of weak organic acids by polyamide 6,6.

The mobility of ions in water is determined by the size of the hydration shell which is greater for ions with a smaller crystallographic radius. However, the mobility of cations in moderately hydrophilic polymers diminishes with decrease of the crystallographic radius.[42] This fact shows that the cations present in the polymer lack a hydration shell.

2. The Equilibrium Sorption of Electrolytes

The "equipotential internal solution" model has been one of the first to be proposed for simple inorganic ions sorbed by moderately hydrophilic polymers. According to this model, an electrolyte solution, analogous to the external solution but having a potential $\Delta\phi$ relative to the latter, exists in the polymer:

$$K_p = \bar{c}_{Na}/c_{Na} = c_{Cl}/\bar{c}_{Cl} = \exp[\sinh^{-1}(c_f/2c_{NaCl})], \qquad (15)$$

This equation agrees quite well with experiment at moderate and high electrolyte concentrations in the polymer. At high dilutions, appreciable discrepancies are observed between the experimental and calculated K_p.[43]

In the Gilbert–Ridal theory (see Zaikov et al.,[3] p.189), it is assumed that ions are adsorbed on a limited number of statistically distributed ionogenic groups of the polymer in accordance with the equation

$$\lg\left(\frac{\theta_f}{1-\theta_f}\right) = \lg c_{CA} + \frac{W_p + W_v - e\Delta\varphi}{2.3kT}, \qquad (16)$$

where W_p and W_v are the polarisation and van der Waals interaction energies respectively, e is the electronic charge, and c_{CA} the concentration of the electrolyte.

The ion-exchange model has been proposed by Myagkov and Pakshver (see Zaikov et al., [3] Chapter 5) to account for the sorption of HCl, KCH, naphthalene-2-sulphonic acid, and certain dyes by polyamide 6. This model predicts that

$$\lg[x(x_0-x)^{-1}] = \lg k - 2\,\mathrm{pH},$$

where x_0 and x are the total number of functional groups and the number of such groups bound to the ion respectively and k is the sorption constant.

The models mentioned above make it possible to obtain only a limited agreement between the calculated and experimental data, which is the reason for the development of the Mathieson–Whewell polyelectrolyte model (quoted after Zaikov et al.[3]). The authors of this model postulate that the energy required to remove H^+ from the polymer to the solution depends on the electrostatic and osmotic interactions of the electrolyte in the polymer and on the chemical affinity (the difference between the standard chemical potentials of H^+ in the polymer and in the solution $\Delta\mu_H^0$). For a partly dissociating group in the polymer, the following equation is frequently used:

$$\mathrm{pH} = \mathrm{p}K_A - \lg[(1-\alpha_c)\alpha_c^{-1}] - \frac{0.434}{RT}(zF\Delta\varphi + \Delta\mu_H^0), \qquad (17)$$

where z is the charge on the group, K_A the dissociation constant, T the absolute temperature, F the Faraday, and R the gas constant.

Association of groups bearing unlike charges in the polymer distorts the potential and its distribution in the membrane. There exist two ways of taking into account association. According to the first procedure, a correction coefficient β, characteristing the fraction of charged groups incorporated in the ion pairs (associated species), is introduced in order to describe the potential. In this case the electrostatic factor is determined by the coefficient $-0.0434F\phi_m\beta/RT$, where ϕ_m is the average membrane potential. However, since β is difficult to calculate because it depends on the electrolyte concentration and hence on the coordinate of the diffusion process, it is more convenient to employ two kinds of carboxy-groups (in the general case acid groups)—free and paired, which dissociate with their own dissociation constants K_p and K_q respectively [see Eqn.(17)]. In this case the concept of a homogeneous membrane potential ϕ_m is retained.

The molecular weights of polymers dissociating only at the terminal groups influence the solubility of the electrolyte. If it is assumed that the accessibility of these groups, the pK, and $\Delta\mu_H^0$ are independent of the degree of polymerisation, then Eqns.(15) and (17) make it possible to relate the degree of polymerisation and the content of end groups c_f to the acid concentration:

$$\mathrm{pH} = \mathrm{const} - 0.434\,\sinh^{-1}(c_f/2c_s), \qquad (18)$$

When $c_f/2c_S > 200$, i.e. when the concentration of the added salt c_S is low, $\sinh^{-1}(c_f/2c_S)$ can be replaced by the corresponding logarithmic relation:

$$\mathrm{pH} = \mathrm{const} - \ln(c_f/c_s). \qquad (19)$$

Graphical solution of Eqn.(19) with a constant c_S, which is presented in Fig.5, indicates a satisfactory agreement between theory and experiment.

In the absence of specific interaction, titration curves make it possible to estimate the pK of the acid groups of the polymer. For example, for keratin twice the pH at the midpoint of the titration curve (i.e. on the plot of pH against $\bar{c}_{HA}$) is equal to the pK of glutamic acid, which can serve as a model of the elementary unit of this polymer. However, for adipic acid, the model of the elementary unit of polyamide 6,6, such an equaltity has not been observed even if a correction is made for the shift of the isoelectric point of this polymer as a consequence of the inequality of the numbers of its acid and basic groups. The most probable cause of this discrepancy is a lower dielectric constant ε in polyamide 6,6 compared with the keratin matrix, where ε does not differ markedly from its value in water.

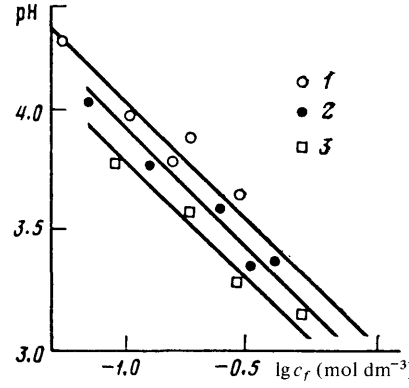


Figure 5. The influence of the degree of polymerisation (of the content of end groups) on the pH in the PA–HCl system for different degrees of ionisation: 1) 0.7; 2) 0.6; 3) 0.5.[3]

Table 5. Diffusion coefficients (D), activation energies for diffusion (E_D), changes in the chemical potential ($\Delta\mu$), and heats of sorption (ΔH) of organic acids in polyamides 6,6 at 60 °C (see Zaikov et al., [3] Chapter 5).

Acid	$10^{13}D$, m^{2}s^{-1}	E_D, kcal mol^{-1}	$\Delta\mu$, kcal mol^{-1}	ΔH, kcal mol^{-1}
Formic	13.2	2.8	0.18	0.4
Acetic	18.1	7.7	−0.41	−0.4
Propionic	14.4	7.2	−0.42	−0.24
Butyric	10.0	6.9	−0.41	−0.70
Salicylic	2.7	21	−1.8	−1.9
Benzoic*	0.3	12.9	—	−3.2
Sorbic**	2.6	3.1	−1.9	−9.8

*Polyamide 610, temperature 45 °C.
**Temperature 55 °C.

Table 5 lists the chemical affinities $\Delta\mu$ of various acids for the polymer, calculated by Eqn.(17). Apart from their theoretical interest, these results are of practical value for the estimation of the stabilities of dyed articles.

IV. DIFFUSION IN HYDROPHOBIC POLYMERS

Polymers of this class are characterised by a high chemical stability in relation to electrolyte solutions. The low polarity of their macromolecules is responsible for the low solubility

of water and electrolytes in hydrophobic polymers, for example, in polyolefins, polyesters, and fluorinated plastics (PTFE). As a consequence of the low polarity of the polymer medium, the acids, bases, and salts contained in it are associated. In this connection, one may note that polymers resistant to acid hydrolysis are as a rule hydrophobic; however, the opposite claim is invalid, because not every hydrophobic polymer is resistant to acid hydrolysis. An example of this is provided by polysiloxanes (see Zaikov et al.,[3] p.147).

1. The Influence of the Nature of the Electrolyte

The most characteristic feature of the diffusional transport of electrolytes in hydrophobic polymers is its selectivity. For example, the permeation of nitric acid through a film of ftoroplast-42 (a type of PTFE) is recorded after ~10^3 s, while the permeation of sulphuric acid through a similar film can be observed only after a year.[44]

Almost all hydrophobic polymers are readily permeable to hydrochloric, hydrofluoric, nitric, acetic, and fluorosilicic acids and to ammonium hydroxide solutions. Sulphuric and phosphoric acids, inorganic bases, and salts diffuse much more slowly (see Reitlinger,[4] p.45). For a series of electrolytes, for example in the polypropylene–KCl system,[47] the permeability could not be measured at all apparently owing to the low solubility of the electrolyte and the inadequate sensitivity of the method of measurement.

The permeability of hydrophobic polymers and the vapour pressures of the electrolytes were first compared by Shterenzon and co-workers.[47,48] Electrolytes characterised by a high vapour pressure diffuse into polymers with coefficients close to the diffusion coefficients of water (D_{H_2O}). Another group of electrolytes, having low volatilities, is transported in polymers with diffusion coefficients much lower than those of water in the same polymer. An analogous classification of electrolytes into "strongly diffusing" and "weakly diffusing" has been proposed by Alt.[49] It is important to note the arbitrary nature of the subdivision of electrolytes into volatile and involatile. At high temperatures and concentrations a typical involatile electrolyte such as sulphuric acid behaves as a volatile electrolyte as regards transport.

The influence of the nature of the volatile electrolyte on its diffusion coefficient is non-specific and is expressed solely by the dependence of the diffusion coefficient on the size of the diffusing species (see Zaikov et al.,[3] p.155).

The concentration dependence of the diffusion coefficient of HCl in low-density polyethylene (LDPE) has been investigated with the latter in contact both with a dry gas at different partial pressures and with an aqueous solution.[50] It was noted that the integral diffusion coefficients of hydrogen chloride diffusing from aqueous solutions increase with increasing concentration of hydrochloric acid, tending to the constant value found for the dry gas. In order to account for this result, a comparative study was made of the equilibrium sorption of HCl from a dry gaseous phase and from aqueous solution. At identical vapour pressures, a greater amount of HCl is sorbed from the solution than from the gas phase. This difference has been explained by the fact that, in the presence of water, some of the electrolyte molecules permeating into the polymer are bound in the form of associated species and an additional amount of HCl passes from the solution to the polymer in order to establish an equilibrium. The overall amount of the sorbed acid (c_{HCl}) is in this case determined by the equation

$$c_{HCl} = c_F + MK_H c_F (p_w k_w)^n \qquad (20)$$

where c_F is the concentration of free HCl not bound in the hydrates, M the molecular weight of HCl, K_H the equilibrium constant of the hydrate formation process, k_w the constant for the sorption of water by the polymer, p_w the partial pressure of water vapour over the solution, and n the number of water molecules in the hydrate, which is 5.0 ± 1.3 for the given system.[50]

It is seen from Eqn.(20) that the ratio of the hydrated and unhydrated forms of the acid diminishes with decrease of the partial pressure of water vapour.

The proposed model makes it possible to obtain an expression for the effective diffusion coefficient of HCl in polyethylene and to describe quantitatively its concentration dependence:

$$\bar{D}_{HCl} = \frac{D^0_{HCl}}{1 + MK_H (k_w p_w)^n}, \qquad (21)$$

where D^0_{HCl} is the diffusion coefficient of dry gaseous HCl. The average number of water molecules in the HCl hydrate, calculated from the results of kinetic (diffusion) measurements, is 4.3 ± 1.7, which is fairly close to the values of n obtained from equilibrium sorption data.[50]

The possibility of the existence of hydrates of volatile electrolytes in hydrophobic polymers was pointed out by Dolezel,[51] who observed a sharp increase of D_{HNO_3} in poly(vinyl chloride) in the presence of a 50% concentration of the acid.

Murov et al.[52] proposed a model involving the parallel-consecutive binding of the electrolyte and water in hydrophobic polymers of the type of polyethylene and polypropylene (PP). According to this model, the non-stationary flux of water molecules from dilute solutions of the volatile electrolyte, subject to the condition $p_w \gg p_s$, can exceed the non-stationary flux of the electrolyte (consecutive binding scheme). In this case it is assumed that the electrolyte diffuses in the hydrated polymer matrix and the probability of the existence of free electrolyte molecules is lower the higher the concentration of water in the polymer. With increase of the concentration in the solution in the external phase, the water and the electrolyte vapour pressures become similar ($p_w \cong p_s$) and the components are bound in the polymer in accordance with the parallel kinetic scheme. The transport of unhydrated electrolyte species is in such cases facilitated.

A further development of ideas concerning the interaction of water and the electrolyte in the polymer was achieved by Shterenzon (see Zaikov et al.,[3] p.159). If it is assumed that the composition of the hydrated complex $HA \cdot xH_2O$ is analogous to that of the external solution, then

$$\lambda_D^2 = r_0 \left[\frac{p_s}{p_s^0} \left(\frac{p_w}{p_w^0} \right)^x \right]^a \qquad (22)$$

where λ_D is the non-stationary permeability coefficient,[3] reflecting the rate of movement of the diffusion front of the electrolyte in the polymer, p_w^0 and p_s^0 are the vapour pressures of the pure electrolyte and pure water respectively, r_0 and a are empirical constants, and x is the number of moles of water per mole of the acid.

The calculated and experimental values of λ_D agreed satisfactorily over a wide range of HCl, HF, HNO_3, and H_2SiF_6 concentrations. Here it is appropriate to emphasise that the concentration dependence of λ_D(HCl) has the same form in dilute (7%) and concentrated (29%) solutions, which makes it possible to put forward the hypothesis of a transition of the diffusion mechanism from consecutive to parallel binding.

2. The Influence of the Nature of the Polymer

The chemical structure of hydrophobic polymers influences only weakly the rate of diffusional transport. In most cases the difference between the diffusion parameters is determined by the difference between the morphologies of the polymers. For example, the extremum in the dependence of the sorption of nitric acid by vinylidene fluoride–chlorotrifluoroethylene and vinylidene chloride–hexafluoropropene copolymers on composition can be accounted for by the transformation of the structure into an amorphous form[53] (the permeability constants of the membranes have been published,[15] p.141).

The polar groups present in a polymer as a result of oxidation alter significantly the diffusion characteristics of hydrophobic polymers. It has been shown,[54] that, with increase of the concentration of the carbonyl groups in polyethylene on oxidation, its electrical conductivity and sorption capacity with respect to salt solutions also increase. Polyethylene films oxidised by sulphur trioxide absorb up to 20% of water and behave like polycarboxylic acid, manifesting, in particular, ion-exchange properties.

The introduction of a filler into the polymer matrix can decrease the mobility of the macromolecules and can lead to the appearance of defects in the polymeric diffusion medium and to the direct interaction of the diffusing species with the additives. Polyethylene containing 16% of graphite, which is inert with respect to the polymer and the electrolyte, is 10% less permeable than unfilled polyethylene. The introduction of a filler without a high adhesion capacity towards the polymer, namely chromium oxide, does not decrease but actually increases the rate of diffusion of HCl and especially HF. Dyeing of a chlororubber coating with TiO_2 also entails an increase of its permeability to Cl^- ions.[55] Zaikov et al.[3] (Chapter 6) have reviewed investigations of the interaction of electrolyte components with the additives introduced into a hydrophobic polymer (hydrophilic fillers of the type of talc and CaO, various surfactants, and plasticisers).

Table 6. The activation energies for the diffusion of electrolytes (Zaikov et al.,[3] Chapter 6).

Polymer	Electrolyte	c, wt.%	E_D, kJ mol^{-1}
Poly(ethylene terephthalate)	H_2SO_4	53	50
PTFE	HNO_3	98	18.8 (>323 K) 50.6 (<323 K)
PE	HNO_3	98	41.8
PE	H_2SO_4	10	55
PP	H_2SO_4	10	31

3. The Influence of Temperature

For many of the systems investigated, a linear relation has been observed between $\lg D_S$ and $1/T$, which makes it possible to calculate the activation energy for diffusion E_D (Table 6). A characteristic feature of the diffusion of electrolytes in polymers is manifested by the fact that the diffusion parameters are determined simultaneously by the electrolyte concentration in the polymer and the experimental temperature. It has been reported[56] that, for a non-steady state process involving the permeation of HCl into high-density polyethylene, E_D varies from 49.3 to 39 kJ mol^{-1} with increase in the concentration of the acid from 15 to 30 wt.%. An empirical equation for the dependence of the non-stationary permeation coefficient λ_D on temperature and concentration (pressure) of the electrolyte has the following form:

$$\lambda_D = A_0 e^{(U/RT)}, \quad (23)$$

where A_0 is an empirical parameter which depends on the concentration or vapour pressure of the electrolyte and U is the energy parameter. Here it is important to note that the pre-exponential factor depends on concentration and temperature (see Zaikov et al.,[3] p.161), which has been confirmed by a series of experiments.[57]

4. The Interaction of Diffusion Fluxes. Countercurrent Diffusion

The interaction of the diffusion fluxes of water and the electrolyte is manifested by the desorption of the latter into water from hydrophobic specimens. Thus a polyethylene specimen subjected to preliminary saturation with hydrochloric acid desorbs HCl into an aqueous environment extremely slowly, while the desorption in a stream of dry air is significantly faster. A detailed study[58] has been made of the phenomenon of the temporary cessation of the release of acid from the film under the conditions of the countercurrent diffusion of water. The interaction of water and the acid in the polymer increases the delay time θ and hence leads to unjustifiably low diffusion coefficients $D = l^2/6\theta$, where l is the thickness of the polymer film. Extrapolation of $\lg \theta$ to zero water vapour pressure p_W is therefore of considerable interest, since it makes it possible to estimate θ for the electrolyte without taking into account the binding to water.[12]

When hydrophobic polymers are used as protective coatings, the specimens become turbid in the presence of many electrolytes. The appearance of turbidity is initially very rapid and then slows down, taking place over a period of several tens and hundreds of hours. The intensity of the turbidity depends on the nature of the polymer and the electrolyte and also on the concentration of the latter. Sulphuric, phosphoric, and acetic acids and ammonia do not cause turbidity, while the countercurrent diffusion of hydrochloric, nitric, and hydrofluoric acids in the region of an ~30% concentration leads to the formation of the electrolyte solution phase in the case of LPPE.[47]

Just as a mist is formed in the gas phase, in hydrophobic polymers there is a possibility of the appearance of tiny droplets resulting from the association of the volatile electrolyte with water. However, the formation of a new phase within the polymer requires the expenditure of energy on the deformation of its structure. In polymers with different physicomechanical characteristics, identical expenditures of the energy liberated as a result of the interaction of water and electrolyte lead to the formation of drops of different size. In certain cases the resistance of the polymer to deformation is so great that the new phase cannot be formed.[47] The enthalpy ΔH^0 of the process $(CA)_{gas} \rightleftarrows (CA)_{soln}$ has been suggested as a quantitative criterion of the possibility of forming clusters in hydrophobic polymers.[47] The ΔH^0 for the electrolytes investigated can be arranged in the sequence

$$\Delta H^0_{NH_3} > \Delta H^0_{HNO_3} > \Delta H^0_{HCl} > \Delta H^0_{NH_4Cl}.$$

In the countercurrent diffusion of water and ammonia, the liberated energy (10 kJ mol^{-1}) is insufficient for the formation of drops, while the energy evolved as a result of the interaction of the HCl and ammonia fluxes is so great that a

continuous layer of ammonium chloride is formed within the polyethylene film, disrupting the polymer matrix. In practice the above effects are used to obtain X-ray contrast materials and for the layer-by-layer cleavage of polymer membranes in microscopic studies.

5. The Sorption of the Electrolyte

For an approximate estimate of the concentration of the sorbed electrolyte in the amorphous phase of the polymer, it has been suggested[47] that a simplified version of the Flory equation be employed:

$$-\ln \varphi_s = 1 + \frac{\bar{v}_s (\delta_s - \delta_p)^2}{RT}, \qquad (24)$$

where δ is the solubility parameter, ϕ and $\bar{v}$ are respectively the volume fraction and the molar volume of the ith component, and s and p are subscripts referring to the electrolyte and the polymer respectively. Eqn.(24) shows that the degree of equilibrium sorption of the electrolyte is greater the lower the modulus of the difference between the solubility parameters of the polymer and the electrolyte. For polyolefins $\delta_p = 16$, for pentaplast $\delta_p = 10$, and for sulphuric acid $\delta_s = 35$ $J^{1/2}cm^{-3/2}$. It follows from Eqn.(24) that the concentration of H_2SO_4 in pentaplast should exceed the concentration of acid in polyolefins by a factor of 40. The different permeabilities of pentaplast and polyethylene to H_2SO_4 indirectly support this.[3]

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A quantitative description of the diffusion and solubility of electrolytes in polymers is an essential condition for the prediction of the chemical stability of the material and of the operating parameters of anticorrosion coatings (hydrophobic polymers). For the successful employment of medical polymers as implants and elements of artificial organs, information is also required about the equilibrium and kinetic parameters for the sorption of the components of the biological medium (on hydrophilic and moderately hydrophilic polymers). The optimisation of the dyeing and printing processes is impossible without a description of the diffusion in fabric materials.[59] The theory of membrane purification, separation, and concentration methods is also based on the diffusion mechanism in hydrophilic and moderately hydrophilic membranes.[60] One can claim with confidence that in the future our ideas about the diffusion of electrolytes in polymers will expand significantly in connection with the vigorous development of chemotronic systems and photochemical and mechanochemical energy converters.

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Institute of Chemical Physics,
USSR Academy of Sciences,
Moscow