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# Diffusion of Electrolytes in Polymers

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The quantitative aspects of the diffusion of electrolytes in polymers are discussed. Methods of studying diffusion are reviewed. The transport of electrolytes in hydrophilic and in hydrophobic non-ion-exchange polymers is analysed. 179 references.

CONTENTS

I. Introduction 781
II. Characteristics of the diffusion of electrolytes in polymers 781
III. Methods of investigation 782
IV. Hydrophilic polymers 785
V. Hydrophobic polymers 790

## I. INTRODUCTION

The diffusion of electrolytes in polymers has attracted a great deal of attention in recent years because of the theoretical and practical importance of this phenomenon. The prediction of the protective properties of polymer coatings, the permeability of biological membranes and tissues, dialysis in medicine, the desalination of sea water, the purification of sewer waters: all this is only a partial list of the processes in which diffusion plays a crucial role. Furthermore we can establish the mechanism of the degradation of polymers in aggressive media (solutions of electrolytes) only if we know the diffusion parameters and the state of the aggressive medium, i.e. the degree of dissociation and of interaction of the components of the electrolyte solution with the macromolecules and with the water molecules.

The theory used to discuss the diffusional transport of electrolytes treats diffusion systems as quasi-binary. However we must make allowance for a number of factors which are characteristic of the diffusion of electrolytes though they are irrelevant to other diffusants: dissociation into ions, hydration, interaction of flows, etc. A proper understanding of these factors is the main objective of current research on the quantitative description of the diffusion of acids, bases, and salts in polymers.

## II. CHARACTERISTICS OF THE DIFFUSION OF ELECTROLYTES IN POLYMERS

### 1. The Presence of Ions

Electrolytes in a polymeric matrix can dissociate into ions which (unlike neutral particles) can move under the influence of a gradient in electrochemical potential. There are three main approaches to the description of the diffusional transport of electrolytes in polymers: the Nernst–Planck electro-diffusion equations[1,2], the thermodynamics of irreversible processes[3], and the theory of absolute reaction rates[4,5]. In spite of some differences in the description of the transport process (mainly, the treatment of the membrane as a heterogeneous matrix in the theory of absolute rates and the allowance for the interaction of the diffusion flows in the irreversible theory) all these approaches give mutually consistent results.

By definition, a flow of ions of a given kind ($J_i$) can be expressed as

$$J_i = u_i c_i A_i, \tag{1}$$

where $u_i$ is the mobility of the ion (referred to unit force), $c_i$ is its concentration in the polymer, and $A_i$ is the generalised driving force of the transport process. Combining Eqn. (1) with the Nernst–Einstein expression for the electrochemical potential

$$D_i = u_i RT \tag{2}$$

and equating concentrations to activities we arrive at the basic Nernst–Planck equation for the diffusion of ions

$$J_i = -D_i c_i \left[ \frac{1}{c_i} \frac{dc_i}{dx} + \frac{\bar{V}_i}{RT} \frac{dp}{dx} + \frac{z_i F}{RT} \frac{d\psi}{dx} \right]; \tag{3}$$

where $\bar{V}_i$ is the partial molar volume of the ion $i$, $z_i$ is its charge, $dp/dx$ and $d\psi/dx$ are the pressure gradient and the gradient of diffusion potential in the membrane respectively, $T$ is temperature, $R$ and $F$ are the gas constant and the Faraday respectively.

In the absence of mobile or fixed charges, and of pressure gradients, Eqn. (3) is equivalent to the formulation of Fick's first law for a binary system of non-electrolytes. In the case of multicomponent diffusion a system of equations of type (3) can be solved by introducing the electroneutrality condition in the absence of electric current and of pressure gradients. In the simplest case (diffusion of a 1–1 fully dissociated electrolyte) the diffusion coefficient ($D_{AC}$) and the gradient of diffusion potential are given by

$$D_{AC} = \frac{D_A D_C}{D_A + D_C}; \quad \frac{d\psi}{dx} = -\frac{RT}{F} \left( \frac{u_C - u_A}{u_C + u_A} \right), \tag{4}$$

where $D_i$ and $u_i$ are the diffusion coefficient and the mobility of the cation (C) and of the anion (A) in the polymer. The diffusion coefficient of a partially dissociated electrolyte can be expressed as

$$D = [\alpha D_{AC} + 2(1-\alpha) D_n] \left( 1 + \frac{d \ln y_\pm}{d \ln c} \right), \tag{5}$$

where $\alpha$ is the degree of dissociation of the electrolyte in the polymer, $D_n$ is the diffusion coefficient of the neutral molecule, $y_\pm$ is the activity coefficient of the electrolyte, and $c$ is the concentration of electrolyte in the polymer[6].

### 2. Allowance for Several Components

Experimental data for $n$-component diffusion systems show that each of the independent diffusion flows is a linear function of all the independent concentration gradients. According to the Gibbs–Duhem equation we can have $n - 1$ independent concentration gradients in such a system, giving rise to an equal number of diffusion flows. A full treatment of diffusion by irreversible thermodynamics involves the determination of $(n - 1)^2$ diffusion coefficients, which is a difficult experimental problem.

However in the diffusion of electrolytes the number of freely moving particles ($N_0$) is not necessarily equal to the number of components: it is given by the expression

$$N_0 = H + n_i - R_0 - 1, \quad (6)$$

where $H$ is the number of types of independently mobile neutral molecules (including water, polymer, etc.), equal to the difference between the total number of types of uncharged molecules and the number of possible reactions between them, $n_i$ is the number of electrolyte ions, and $R_0$ is the number of ionic reactions[3].

In order to satisfy the Onsager relation[7], which postulates equality of the cross diffusion coefficients, the number of independent $D_i$ coefficients describing the diffusion of $N_0$ independently moving components must be decreased to

$$D_i = \frac{1}{2} N_0 (N_0 - 1). \quad (7)$$

The determination of a large number of diffusion coefficients in a multicomponent system requires a great deal of diffusion and thermodynamic information, which is seldom available. We usually have to rely on various simplifying assumptions on the relationship between the various diffusion coefficients and on the distribution of component concentrations in the system (see, for example, Refs. 7–9). Multicomponent diffusion is described most exactly by the Stefan–Maxwell equations, which are applied to transport phenomena in gases[10]. In biological systems and in reverse osmosis experiments diffusion is usually described by the Kedem–Katchalsky equations[10,11].

### 3. Choice of a Characteristic Diffusion System

The overall flow of any diffusing component with respect to an arbitrary system of coordinates ($J_{0i}$) can be expressed as the sum of a convective flow, due to the motion of the system as a whole with velocity $w_s$, and a true diffusion flow, measured relatively to the convective flow:

$$J_{0i} = w_s c_i + J_i. \quad (8)$$

The choice of a characteristic velocity depends on the properties of the system and on the method of investigation. The following characteristic systems are most commonly used: the Fick characteristic system, based on measurements of the mean volume velocity, 2) the Hittorf characteristic system, based on measuring the velocity of any one component (for example, the solvent) in the membrane, 3) the centre of mass characteristic system, based on measuring the velocity of the centre of mass, and 4) the lattice characteristic system, based on measuring the rate of displacement of the lattice sites in the crystal. The relationship between the flows and the diffusion coefficients in the various systems is discussed in detail in Ref. 3 (p. 239) and in Ref. 12.

### 4. Effect of an Unstirred Layer of Electrolyte Solution

When an electrolyte is diffusing in a polymer we often have to consider the effect of a liquid film of solution in contact with the polymer surface and adhering to that surface even when the system is stirred. This immobile layer, called the Nernst layer (see Ref. 2, p. 129), is found in all multicomponent systems. Allowance for the retardation of diffusion near the polymer surface is essential in the case of hydrophilic polymers with a high water content.

The criteria which determine whether the fixed layer can be ignored are discussed by Helfferich[13]. The transport of solute through a polymer membrane in the presence of a Nernst layer is described by the equation

$$J = -Dc\left[l\left(1 + \frac{2cl_N D}{D_N c_N l}\right)\right]^{-1}, \quad (9)$$

where $l_N$ is the thickness of the Nernst layer, $l$ is the thickness of the polymer, and the parameters with the subscript N refer to the solution in which the polymer is immersed. It follows from Eqn. (9) that for $D_N c_N l \gg Dcl_N$ the diffusion process is controlled by the polymer membrane, and for $Dcl_N \gg D_N c_N l$ the Nernst layer is rate-limiting.

The measurement of the thickness of the fixed layer is a difficult experimental problem. Peterson and Gregor[14] have calculated $l_N$ as a function of the stirring rate by combining Eqn. (9) with indirect kinetic measurements. They found that $l_N$ decreases by more than an order of magnitude as the stirring rate is increased. Other methods of measuring the thickness of the liquid layer include a new procedure[15] based on the current–voltage characteristics of the membrane. Measurements of $l_N$ for spherical samples are described in Ref. 16.

### 5. Interaction Between the Electrolyte and the Polymer

If the polymer contains inorganic groups, strong interactions can occur between these groups and the diffusing electrolytes. A typical example of this behaviour is found in the aqueous electrolyte–polyamide system, discussed below. In polymers which are practically free from polar groups (polyethylene, polypropylene) the interactions between the diffusing components are predominant.

At present there is no general quantitative theory relating the structural parameters of the polymer to the diffusion coefficients of electrolytes within that polymer. An analysis of the diffusion of various electrolytes suggests that polymers can conveniently be classified into three groups according to their water content: polymers which easily dissolve water ($> 10$ wt.%), polymers in which the solubility of water is limited, and polymers which dissolve very little water ($< 1$ wt.%). The polymers of the first group are hydrophilic, the others are hydrophobic.

## III. METHODS OF INVESTIGATION

### 1. Methods Based on Measuring the Permeability of the Polymer

The determination of diffusion parameters by measuring permeability consists in measuring the amount of electrolyte transported in unit time through unit area of the polymer film. The diffusion coefficients can be calculated

from data on the rate of transport under steady-state conditions and on the solubility of the electrolyte in the polymer by integrating Fick's equation

$$\bar{D} = q(c_0)\, l/(c_0 - c_p), \qquad (10)$$

where $\bar{D}$ is the integral diffusion coefficient[17], $q(c_0)$ is the rate of transport, and $c_0$ and $c_p$ are the concentrations of electrolyte in the surface layer of the polymer on the side of the diffusion source (usually assumed to be equal to the solubility in the polymer) and on the side of the detector cell respectively. Under most experimental conditions $c_0 \gg c_p$, which simplifies Eqn. (10). We should note that the calculation of diffusion coefficients by this equation can lead to low values because the quantity $c_0$ as determined from solubility measurements includes both mobile and immobile (strongly sorbed) forms of the electrolyte[17].

Another method of calculating diffusion coefficients is based on the Frisch equation[18], which in the case of concentration-independent diffusion coefficients reduces to the well known Dienes–Barrer equation

$$D_\theta = l^2/6\theta, \qquad (11)$$

where $\theta$ is the time-lag for the electrolyte–polymer system. In general, when $D$ is a function of concentration, it can be expressed in terms of the directly measurable parameters $\theta$ and $\bar{P}$ (the permeability)[19]:

$$D_\theta = l^2\left[6\theta + 6\frac{d\theta}{d\bar{P}}\bar{P} + \frac{d^2\theta}{d\bar{P}^2}\bar{P}^2\right]^{-1}. \qquad (12)$$

At temperatures above the glass transition point of the polymer, and in the absence of interactions between the diffusing components, the diffusion parameters determined from the stationary and the non-stationary region of the kinetic curve are usually in good agreement over a wide range of concentration[20]. A variety of measuring cells can be used for the measurement of diffusion coefficients; the apparatus usually consists of two cells separated by the experimental polymer. The measuring cell contains a sensor which detects the arrival of electrolyte by diffusion through the polymer. Various methods of detection have been used: electrical conductivity[21,22], pH measurements[23–25], radioactive isotopes[26–29], chemical analysis[30–33], and optical methods[34]. Some of these methods give a direct measurement of the stationary concentration gradient of electrolyte in the polymer during diffusion. These include the layer removal method[35–37] and the multifilm method[38,39]. Knowing the concentration gradient and the flow of electrolyte we can calculate the diffusion coefficient, but in all these methods some uncertainty arises from the possibility of abnormal effects at the boundaries of the various layers.

Methods based on the measurement of permeability are fairly precise and convenient, but they suffer from the following complications. 1) Interactions between the flows of diffusing species. For example, it has been reported[40] that both the permeability and $\theta$ can vary during the counter-diffusion of water and electrolyte, and furthermore a new phase appears within the polymer. 2) Discrepancies between stationary and non-stationary diffusion coefficients. Usually $\bar{D} > D\theta$,[20] which may be due either to relaxation processes in the polymer occurring at a rate comparable to the rate of diffusion or to specific interactions such as water–oxygen interactions in hydrophobic polymers (see below). 3) The samples must be free from interconnected micropores and cracks, which would lead to erroneous results by allowing phase flow.

## 2. Methods Based on Measurements of the Properties of the Polymer–Electrolyte System

The measurement of diffusion parameters by these methods relies on directly or indirectly monitoring the amount of electrolyte in the polymer as a function of time. The equations describing the sorption kinetics for different initial and boundary conditions are discussed in Ref. 41, which also describes the effect of sample geometry on sorption.

To keep the boundary conditions constant during sorption the amount of diffusant in the solution should be much greater than the maximum sorption in the polymer[41]. The following methods can be used to determine the diffusion coefficients of electrolytes in polymers.

Gravimetric method. This method can be used when the sorption of the different components occurs at widely different rates. Concentration is monitored by the methods listed in the previous section. Complications may arise from interactions between solvent and electrolyte flows. The best results are obtained in studies of volatile electrolytes, whose concentration is determined by desorption into the gas phase in a stream of inert carrier gas[42].

Radioactive isotope methods. These methods are very convenient not only for measuring diffusion coefficients but also for measuring the self-diffusion of individual ions and of associated molecules of the electrolyte.

An interesting application is the measurement of diffusion parameters by isotope exchange reactions in the diffusion-limited regime. The course of the reaction (for example, H–D exchange) can also be monitored by i.r. spectroscopy[43].

Spectral methods. The concentration of diffusant in the polymer can be determined by modern spectral methods: optical[44], NMR[45,46], ESR (if the diffusant is paramagnetic[47,48]), and spin-echo[49].

Electrical conductivity method. Four types of conduction are possible in a polymer under the influence of an electric field: ionic, protonic, electronic, and induced. The first two types are the most important during the diffusion of electrolyte solutions.

A full analysis of the conduction processes requires a knowledge of the extent of dissociation of the electrolyte, its hydration, and its interaction with the polymer. The difficulty of obtaining this information is obvious, and therefore the relationship between diffusion coefficients and electrical conductivity is seldom unambiguous over a wide range of experimental conditions[50]. For example, a transition from the ionic to the electronic mechanism of charge transfer occurs as the water content of the polymer decreases[51]. Temperature has a marked effect on electrical conductivity[52].

In many polymers (especially in hydrogels) we can expect Kohlrausch's law of independent migration of ions to apply:

$$\chi = \sum_i z_i c_i u_i \qquad (13)$$

where $\chi$ is the specific conductance and $\mu_i$ is the mobility of the ions in an electric field. If Eqn. (13) applies the integral diffusion coefficient of the ion in the polymer ($\bar{D}_i$) can be calculated by the expression

$$R_e^{-1} = \frac{z_i^2 F^2}{RT} c_{pi}\left[\left(\frac{2l_N}{D_N} + \frac{l}{K_i D_i}\right)\right]^{-1}, \qquad (14)$$

where $R_e$ is the electrical resistance of a sample of unit cross-sectional area and length $l$, $c_{pi}$ is the concentration of the ion in solution, $l_N$ is the thickness of the unstirred layer, and $K_i$ is the distribution coefficient of the ion between the polymer and the solution[1]. If we can ignore the resistance of the Nernst layer Eqn. (14) simplifies to

$$R_e^{-1} = \frac{(z_i F)^2}{RT} \frac{c_{pi} D_i k_i}{l} . \quad (15)$$

The electrical conductivity is a sensitive function of both the strength and the frequency of the applied electric field. As we increase the voltage the ionic transport process is increasingly limited by the unstirred layers at the surface (rather than by the bulk of the membrane), because the conductivity of the membrane increases sharply with field. At low a.c. frequencies the conductivity is determined by the diffusion-induced polarisation of the unstirred layers. At high frequencies the relationship between the diffusion parameters and the electrical conductivity becomes more complex, because under these conditions the ions do not move across the membrane but merely oscillate within a small region.

The methods of determining mobility from electrical conductivity data have recently been reviewed[1,53]. Correct results are obtained with dilute solutions of electrolytes in porous[54] and in charged polymers[55]. As the concentration of the electrolyte increases the concentration dependence of the conductivity becomes non-linear because of the following effects: the increased potential step at the polymer–solution interface, the increased electro-osmotic flow of the solvent, and the increased relaxation effect[56].

The electrical conductivity of polymer membranes is measured by applying electrodes, which can be classified[57] into three groups: electrodes not in contact with the membrane, platinum electrodes, and mercury electrodes. Mercury electrodes appear to be the best, whereas electrodes of the second group give low results and those of the first group give high results. The methods and circuits used in measuring electrical conductivity are described in Refs. 58 and 59.

Other methods used to measure diffusion parameters include micro-hardness methods[60] and the ion-selective electrode method[61], which has been applied to biological systems.

### 3. Methods Based on Monitoring the Moving Boundary of Electrolyte in the Polymer

A characteristic form of micro-motion has been observed during studies of diffusion in systems including a polymer and a low-molecular substance: the motion of a diffusion front into the bulk of the polymer. The mean diffusion velocity of the particles is related to the observed macroscopic motion of these particles by Eqn. (8). In practice the rate of displacement of the electrolyte is measured with respect to the surface of the polymer, and therefore Fick's equation is conveniently expressed in terms of the characteristic Hittorf system (see Chapter II) with $w_S = 0$. For a relatively low concentration of diffusant in the polymer the solution of the continuity equation for this system

$$c_i = c_0 \left(1 - \operatorname{erf}\left[\frac{x}{2(Dt)^{1/2}}\right]\right) \quad (16)$$

applies to a semi-infinite solid bounded by a plane at $x = 0$ and having initial ($c = 0$ for $x > 0, t = 0$) and boundary conditions ($c = c_0$ for $x = 0$, $t > 0$). Assuming that $c/c_0 = \text{const}$, i.e. monitoring the motion of a fixed concentration $c = c_x$, we obtain

$$x = \lambda t^{1/2}; \quad (17)$$

where $x$ is the depth of permeation of a boundary of diffusant of constant concentration $c_x$ in time $t$, and $\lambda$ is the permeation coefficient. The depth of permeation of the diffusant in the polymer can be determined by a variety of methods: autoradiographic[62], optical[63], interferometric[64], or by acid–base indicators[65].

The latter method is the most widely used, but it is difficult to apply to the polymer–electrolyte system. Two types of result have been reported in the literature: 1) different indicators change colour at almost the same value of $x$ (suggesting an anomalous distribution of diffusant in the polymer (steep front), or that the chosen indicators have similar p$K$ values), and 2) the colour change of different indicators occurs at different values of $x$. From these results we can determine the true distribution of diffusant in the polymer only if the relationship of the p$K$ values of the indicators in the polymer matrix to those in water has been established by independent experiments. The concentration gradient of the electrolyte is assumed to be not very steep, so that the colour changes of indicators with different p$K$ in the polymer will occur in different regions of the $c$–$x$ curve. Thus the observed depth of permeation should be a function of the type of indicator used.

In organic solvents the mechanism of the colour change of the indicator is seldom known, and the p$K$ values have not been determined. Furthermore the transition from aqueous to non-aqueous or mixed solvents often causes inversion of the p$K$ values. For example, the colour change of Methyl Red in water occurs at a higher pH than that of Bromophenol Blue, but in alcoholic solutions the opposite is true. Since acids and bases in polymers can be treated (to a first approximation) as mixed solutions, all the uncertainties associated with the use of indicators in non-aqueous and mixed solvents apply to our system. Therefore, with rare exceptions (e.g. gels) the method of acid–base indicators cannot be used to measure the concentration of an acid or a base in a polymer matrix. We can only conclude that the concentration of acid in the coloured part of the resin is greater than in the colourless part.

Because of the difficulty of measuring concentration in a polymer many workers confine themselves to determining the "depth of permeation" at some time $\tau$, or they use the poorly substantiated expression

$$D = x^2/a\tau, \quad (18)$$

where $a$ is an arbitrary number.

We should stress that the use of this formula can lead to an incorrect treatment of the often reported concentration dependence of the diffusion coefficient. It is better to use Eqn. (17), and to express the variation of $\lambda$ with concentration by Eqn. (16).

Mention must be made of a method of correctly determining diffusion coefficients from the velocity of a diffusant front of constant concentration without a knowledge of $c_x$ and $c_0$ (see Ref. 50, p. 209).

The description of the diffusion process becomes even more complicated in the presence of interactions between the electrolyte and the solvent, or of relaxation processes leading to a rearrangement of the polymer structure. These effects will be considered below.

## IV. HYDROPHILIC POLYMERS

Hydrophilic polymers include those in which water is easily soluble [poly(vinyl alcohol) PVA, cellulose, etc.) and those in which water has a moderate solubility (polyamides, some polyesters, etc.). The diffusion of electrolyte in ion-exchange polymers has been studied in great detail, and several monographs on this topic have recently been published[2,13,66]. It is not the purpose of this review to discuss specifically the processes which occur in ion-exchange polymers, but we shall nevertheless examine some of their basic features when the conclusions are equally applicable to non-ion-exchange polymers.

### 1. State of the Electrolyte in Polymers

Some attempts to measure pH in a resin phase have been based on doubtful assumptions. One estimate[67] was made from the colour change of an indicator sorbed by the resin, another[68] by measuring the degree of dissociation of amino-acids in an adsorbed state. The results show a large difference between the pH values in solution and in the polymer, but they cannot be used to evaluate the dissociation constants of the ionogenic groups.

Three methods of determining the dissociation constants of electrolytes in polymers by applying the law of mass action are known: the spectrophotometric method[69,70], the sorption method[71], and the conductimetric method[69].

**Table 1.** Dissociation constants of electrolytes in polymers containing 60–70 wt.% of water ($pK_1$ is quoted for ampholytes).

| System | $pK_{diss}$ | References |
|---|---|---|
| PVA - $H_3PO_4$ | 3.1 | 69 |
| PVA - *m*-nitroaniline | 2.6 | 69 |
| Dowex-50 - *m*-nitroaniline | 2.5 | 70 |
| Sulphonated polystyrene - glycine | 2.5 | 71 |
| KU-2 x 4 - glycine | 2.3 | 71 |
| KU-2 - glutamic acid | 2.2 | 71 |

Dissociation constants measured in various polymer–electrolyte systems are listed in Table 1. The $pK$ values are close to the corresponding values for aqueous solutions. The small difference between the $pK$ values in the resin and in solution is explained by selective absorption of one of the forms of the sorbed electrolyte. For example, in the case of aliphatic amino-acids the selectivity of the resin towards the univalent cation is small, and not very different from the selectivity towards the zwitter-ion: hence the $pK$ of the acid in the polymer is practically the same as in water. The selectivity for bivalent cations is higher as a result of the electrostatic interaction with the charged groups of the resin, and the dissociation of the amino-acid is displaced towards the formation of the bivalent cation[71]. The equality of the $pK_1$ values of phosphoric acid in poly(vinyl alcohol) and in water can be explained either by the presence of micropores in the polymer, allowing access to the aqueous solution[72], or by the formation in the polymeric alcohol of structures having the same affinity towards the ions as the aqueous solution.

We note that in the PVA–$H_2O$–KCl system (in the same concentration range) the dielectric constant (which influences the dissociation of the electrolyte) is lower than in water by a factor of two, whereas the kinetic parameter (electrical conductivity) is an order of magnitude lower[73].

The dissociation of sulphuric acid in polycaproamide has been studied by an electrical conductivity method[74]. By making a number of assumptions the authors concluded that sulphuric acid can dissociate in the polymer containing as little as 6% of water. Only the first ionisation is significant, with $pK_1 = 2.5$.

The behaviour of ions is largely determined by their hydration. It has been shown[75] that the self-diffusion coefficients of the alkali metal cations in sulphonated polystyrenes increase in the sequence $Li < Na < K < Rb < Cs$, in qualitative agreement with the radii of the hydrated cations. The influence of hydration on the self-diffusion of ions in these polymers is confirmed by the relative values of the self-diffusion coefficients of multivalent ions ($Th^{4+} < In^{3+} < Ca^{2+} < Na^{+}$), since it is well known that the number of water molecules in the hydration shell of an ion increases with the valency of the ion.

On increasing the parameter which characterises the stability of the hydration shell of anions $(z_i/(r_i - 0.25)$, where $r_i$ is the crystallographic radius of the ion) a proportionate decrease was observed in the ability of salts to diffuse into cellulose acetates ($NaNO_3 > NaCl > NaF > Na_2SO_4$), accompanied by a change in selectivity in the opposite sense[77].

### 2. Main Theories of the Diffusion of Electrolytes in Polymers

The following theories have been proposed to explain the diffusion of electrolytes in polymers.

The **Mackie and Mears theory**[78] ascribes the lower diffusion coefficients of electrolytes in hydrophilic polymers (as compared with aqueous solutions) to the increased diffusion path produced by the presence of the macromolecules. In the absence of interaction between the functional groups of the polymer and the ions this effect can be allowed for by introducing the factor $[(1 + \varphi_2)/(1 - \varphi_2)]^2$, where $\varphi_2$ is the volume fraction of the polymer.

The discrepancy between experimental and calculated diffusion coefficients necessitated the introduction of a correction for the difference in viscosity (as compared with aqueous electrolytes)[79]. However the validity of this correction is doubtful because of the ambiguity of the concept of viscosity in polymers[80].

The **Yasuda theory**[81–83] is a development of the free volume theory specifically aimed at hydrophilic polymers. It is assumed that the free volume of a swelled membrane is determined by the mole fraction of solvent ($\varphi_1$). The diffusion coefficient of the electrolyte in the membrane becomes

$$\lg D = \lg D_w - k\varphi_1^{-1}, \qquad (19)$$

where $D_W$ is the diffusion coefficient of the electrolyte in water and $k$ is a proportionality constant related to the volume taken up by the migrating electrolyte and to the free volume of the whole system. Fig. 1 shows a plot of the logarithm of the diffusion coefficient of sodium chloride in copolymers based on polyacrylamide with different amounts of hydroxyl groups against the mole fraction of water in the polymer. Eqn. (19) is not obeyed at low mole

fractions of water. Two important conclusions stem from this theory: 1) in the case of ions we expect a linear plot of $\lg D$ against $\lg D_w - q_i$, where $q_i$ is equivalent to the cross-sectional area of the ion, and 2) the higher the water content of the membrane, the less marked is this relationship.

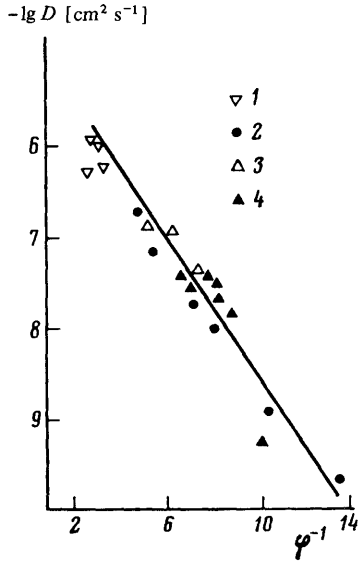



**Figure 1.** Diffusion coefficients in copolymers with different hydroxyl group contents against volume fraction of water in the polymer[81]: 1) hydroxyethyl methacrylate, 2) copolymers of methyl methacrylate with glyceryl methacrylate, 3) ditto with hydroxyethyl methacrylate, 4) ditto with hydroxypropyl methacrylate.

Boyd's approach[84] is a further development of previous theories. The decrease in mobility of ions upon being transferred from water into ion exchange polymers can be explained by three effects: a) the decrease in diffusion cross-section due to steric hindrance by the polymer network, b) the increase in the length of the diffusion path due to the need to avoid the polymer network, and c) interactions with pore walls. The relative importance of these three factors depends on the nature of the polymer and of the diffusant.

The model of Medley[85] and Marshall[86] is used to explain the dependence of the diffusion coefficients on the structure of polymers in which the solubility of water is limited. For example, in contrast to the case of high water solubility, the water dissolved in polyamides cannot form a continuous aqueous environment for the motion of the electrolyte in the polymer matrix. The water exists mainly near the polar end-groups, and to a lesser extent near the amide bonds. The ions diffuse by activated jumps from one polar group to another, passing through regions of low dielectric constant. For example, in polyhexamethylenediamine the distance between two nearest groups having the same charge is 30–40 Å, which probably determines the jump length.

If we assume that polyamides exist in a zwitter-ion form, the active centres for the diffusion of ions are the positively charged amino-groups, and those for the diffusion of protons the carboxyl groups.

Measurements of spin–spin and spin–lattice relaxation times for the polyamide–water system as a function of composition have shown that up to 0.5 wt.% of water can be present as water molecules strongly bound to the amide bonds. When the water content is increased from 0.5 to 8.0 wt.% the mobility of the water molecules in the polymer gradually increases to a level approaching the mobility of free water molecules. Addition of sodium chloride also increases the mobility of the water molecules: this effect is explained[87] by the ability of electrolytes to break down the clusters of $H_2O$ molecules formed in the polymer.

## 3. Concentration Dependence of the Diffusion Coefficient

The most characteristic feature of the diffusion of electrolytes in hydrophilic polymers is the concentration dependence of the diffusion coefficients, which can arise in general from the following factors: a) a change in the degree of dissociation of the electrolyte, b) non-ideality of the thermodynamic behaviour of the polymer–electrolyte system, c) swelling of the polymer, causing increased mobility of the polymer segments, d) binding of the electrolyte by the ionogenic groups of the polymer.

We shall examine each of these factors separately. In practice factors b) and c) can be excluded by studying the diffusion of dilute solutions of electrolytes in polymers free from ionogenic groups and previously saturated with solvent.

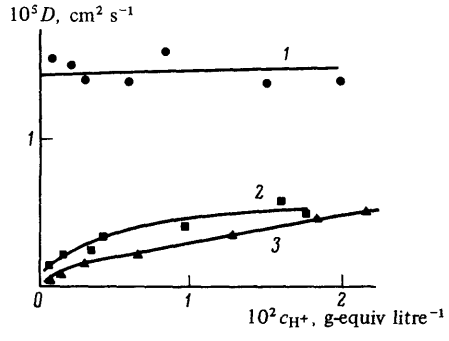



**Figure 2.** Concentration dependence of the diffusion coefficients of acids in PVA[25]: 1) HCl, 2) $H_2SO_4$, 3) $H_3PO_4$.

### a) Concentration dependence of the diffusion coefficient due to changes in the degree of dissociation of the electrolyte

The effect of factors a) and b) stems directly from Eqn. (5). Fig. 2 shows the concentration dependence of the diffusion coefficients of acids in poly(vinyl alcohol) at 25°C. The diffusion coefficients were measured under steady-state conditions from the change in concentration of hydrogen ions in the measuring cell[25].

For a fully dissociated electrolyte (e.g. a dilute solution of HCl) Eqn. (5) can be simplified to

$$\bar{D}=D_{AC}\equiv D_{H^+(Cl^-)}, \qquad (20)$$

Solutions of $H_2SO_4$ of similar concentration show substantial dissociation up to the second ionisation, and hydrogen ions diffuse through the polymer matrix with the counter-ions $HSO_4^-$ and $SO_4^{2-}$. Allowance for dissociation leads to the equation

$$\bar{D}=D_{H^+(HSO_4^-)}\left[1+2\left(\frac{f-2}{[c_{H^+}/K_2+2]^2}\right)\right], \qquad (21)$$

where $c_{H^+}$ is the concentration of hydrogen ions, $K_2$ is the second dissociation constant of sulphuric acid, and $f=D_{H^+}(SO_4^{2-})/D_{H^+}(HSO_4^-)$. In the case of the weaker acid $H_3PO_4$ only the first ionisation is important in this range of concentrations:

$$\bar{D}=D_{H^+(H_2PO_4^-)}\left[1+\frac{2\beta}{K_1}c_{H^+}\right], \qquad (22)$$

where $\beta=D_{H_3PO_4}/D_{H^+}(H_2PO_4^-)$, and $K_1$ is the first ionisation constant of phosphoric acid.

During the diffusion of phosphoric acid in poly(vinyl alcohol) some of the diffusant molecules are bound in the polymer matrix and do not contribute to the mass transfer. In Eqn. (22) all the parameters relate to the free molecules of phosphoric acid.

The concentration of acid bound to the polymer is calculated by the Langmuir equation.

**Table 2.** Diffusion coefficients ($10^6D$, $cm^2\,s^{-1}$) of the ionised forms of acids in PVA and in water[25].

| Ionised form of the acid | PVA | Aqueous solution |
|---|---|---|
| $H^+(Cl^-)$ | 14.4 | 30.0 |
| $H^+(HSO_4^-)$ | 5.9 | 12.0 |
| $H^+(SO_4^{2-})$ | 1.8 | 3.6 |
| $H^+(H_2PO_4^-)$ | 1.2 | 16.1 |

The diffusion coefficients in PVA of HCl, $H_2SO_4$, and $H_3PO_4$ (a strong monobasic acid, a dibasic acid, and a partially dissociated acid) calculated by Eqns. (20) and (22) are given in Table 2. These values are quite close to the diffusion coefficients of the same acids in water. We may conclude that in a polymeric matrix containing 78 vol.% of water the presence of the polymer has little effect on diffusion, because the molecules and the tons of the acid are effectively screened by the water from interactions with the polymer. Hence the only obstacle to diffusion is the need to avoid the PVA macromolecules (except in the region of low concentrations). The theory of Mackie and Mears, which allows for this type of obstacle[78], yields diffusion coefficients close to the experimental values.

The self-diffusion coefficient of the hydrogen ion is approximately an order of magnitude greater than the self-diffusion coefficients of the anions and of the undissociated molecules in PVA.[69] This very high mobility of the proton is difficult to explain in terms of size only, particularly since the protons in the polymer matrix are in a hydrated state. The anomalously high value of $D^0_{H^+}$ is probably due to the specific mechanism of migration of the proton in a hydrophilic matrix, similar to the "relay" mechanism[88].

b) Concentration dependence of the diffusion coefficient due to thermodynamic non-ideality of the polymer–electrolyte system

In the previous section the diffusion of an acid was treated as the diffusion of an electrolyte showing practically ideal thermodynamic behaviour. However as the volume fraction of water decreases we must expect the polymeric molecules to influence the diffusion of the electrolyte, and the system to deviate from thermodynamic ideality. Thus, in the case of a polymer containing 38 vol.% of water the experimental diffusion coefficients of phosphoric acid are different from the values calculated by Eqn. (22). It is reasonable to assume that the difference is due to non-ideality of the diffusion system: in this case we obtain from Eqn. (5) the expression for the mean molar activity coefficient of the ions ($y_\pm$)

$$\lg y_\pm = 0.869\int_0^{c^{1/2}}\frac{D/D^0-1}{v}\,dv, \qquad (23)$$

where $v=c^{1/2}$. Graphical solution of this equation gives $y_\pm$. The results are discussed in Ref. 69.

c) Diffusion complicated by relaxation processes

In polymers close to and below the glass transition temperature the diffusion processes cannot be described in terms of Fick's equations with constant boundary conditions and with a diffusion coefficient depending only on concentration. Diffusion under these conditions is usually termed anomalous.

Anomalous diffusion is characterised by the following criteria[89]: a) the sorption plots of $M_t/M_\infty$ against $t^{1/2}/l$ (where $M_t$ and $M_\infty$ are the amounts of electrolyte sorbed at time $t$ and at equilibrium respectively) are not monotonic, but show characteristic points of inflection or are S-shaped; b) the kinetic sorption curves depend on the thickness of the sample; c) the plots of permeability against time can have maxima or minima in the non-stationary portion, and the time-lag does not obey the modified Frisch equation (12); d) the displacement of the moving boundary of the electrolyte solution is proportional to $t^n$ (where $\frac{1}{2}<n\leqslant 1$) rather than to $t^{1/2}$ [as required by Eqn. (17)].

Several theories have been proposed to describe anomalous diffusion in polymers, but they can all be reduced to two: the molecular relaxation model and the diffusion–convection model[90].

The molecular relaxation model allows for the structural rearrangement of the macromolecules accompanying the penetration of the diffusing species into the polymer matrix[91,92]. At temperatures close to and below the glass transition temperature of the polymer the relaxation times of the molecular segments are similar to (or greater than) the characteristic times of the diffusion process. The case in which the rate of transport is limited only by the relaxation of the macromolecules is often called type II diffusion to distinguish it from diffusion according to Fick's law, which is termed type I diffusion. The criterion for type I diffusion is the applicability of Eqn. (17) to the motion of the diffusant boundary[93].

The effect of molecular relaxation is a time-change (by the first-order equation) in the concentration of diffusant in the surface layer [90,92] or in the diffusion coefficient [91]. For example, the change in surface concentration ($c_t$) with time is described by the equation

$$c_t = c_0 + (c_\infty - c_0)(1 - \exp[-t/\bar{\tau}]), \quad (24)$$

where $c_0$ is the surface concentration of diffusant at $t \to 0$, $c_\infty$ is the equilibrium concentration of the diffusing species in the polymer, and $\bar{\tau}$ is a proportionality coefficient which characterises the mean relaxation time of the macromolecules [94,95].

Solution of Fick's equation with asymmetric boundary conditions [a surface concentration varying according to Eqn. (24)] for steady-state transport leads to the expression [96]

$$\frac{\theta}{l^2} = \frac{1}{6\bar{D}} + \bar{\tau}\left(1 - \frac{c_0}{c_\infty}\right) l^{-2}. \quad (25)$$

Eqn. (25) has the following properties: a) it explains the dependence of the diffusion coefficient $D\theta$ obtained from the non-stationary portion of the permeation curve upon the thickness of the sample; b) it explains the difference between diffusion coefficients determined under stationary and non-stationary conditions respectively; c) it shows that the time-lag experimentally observed in relaxing systems is equal to the sum of the time-lag associated with diffusion by Fick's law and of the time to reach the equilibrium concentration in the surface layer (characterised by the parameter $\bar{\tau}$).

Though the molecular relaxation model can explain a wide range of experimental results it relies on a number of empirical parameters whose physical significance is not always sufficiently clear. Therefore a full understanding of the effects involved in anomalous diffusion is impossible without additional information, obtained independently.

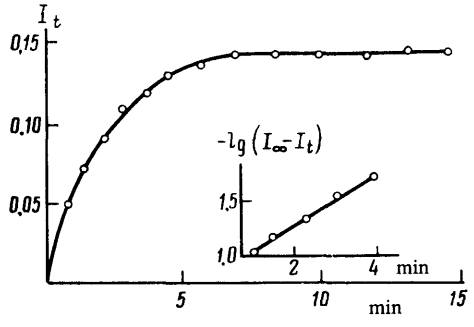



**Figure 3.** Time dependence of the intensity of absorption of an aqueous solution in PVA at 1675 $cm^{-1}$. Insert: graphical solution of Eqn. (24) [99].

The diffusion–convection model applies to strongly swelled glassy polymers. In the limit we observe the motion at constant speed of a sharp front separating the swelled outer layer from the unswelled inner layer [93,97]. In this case the motion of the liquid as a whole, under the influence of various forces, causes transport of the electrolyte dissolved in the liquid at a rate equal to that of the liquid. In some cases the motion of the front of diffusant can occur by an intermediate law,

$$x = \lambda t + \lambda t^{1/2}, \quad (26)$$

which is the sum of Fick's law diffusion and type II diffusion. The diffusion–convection model satisfactorily accounts for the experimental results except when the sorption curves are concave to the time axis [90].

The relaxation and the convection model described above can explain practically any anomalous diffusion phenomenon (except those associated with micro-cracking of the polymer [98]) and, in spite of some lack of physical clarity, they are the only means of describing and interpreting diffusion processes in glassy polymers.

In PVA below $T_g$ we expect the relaxation processes to be slow, and to influence the surface concentration of diffusant. A change in the concentration of the aqueous solution in the surface layer of a PVA film (equivalent to 1% of the total thickness of the film) has been observed experimentally [99] by total internal reflection in the i.r. region. The choice of this thickness of surface layer was arbitrary, and determined primarily by the sensitivity of the measurement. Since a concentration gradient is produced in this layer, the calculation was based on an average concentration $\bar{c}_t$,

$$\bar{c}_t = \int_0^{l_m} c(x)\, dx/l_m,$$

where $l_m$ is the effective depth of penetration of the light beam. The change of $\bar{c}_t$ with time was described by Eqn. (24). Fig. 3 shows the absorption intensity at 1675 $cm^{-1}$ as a function of time for the surface layer of PVA, and a graphical solution of Eqn. (24). The $\bar{\tau}$ values are found to depend on the structure of the polymer.

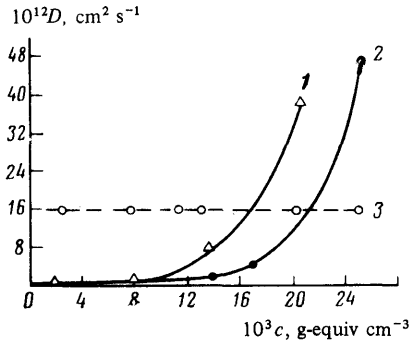



**Figure 4.** Concentration dependence of the diffusion coefficients in a polyamide [86] of: 1) HBr, 2) $H^+$, 3) $Br^-$.

d) Concentration dependence of the diffusion coefficient due to the presence of ionogenic groups in the polymer

The most detailed studies of the concentration dependence of diffusion coefficients relate to the sorption of acids by polyamides. Most workers report a large increase in diffusion coefficient with the concentration of electrolyte in solution [100–108] (see Fig. 4). These results

are explained by assuming that the electrolyte (acid) is sorbed successively by the amino groups and the amido groups of the polyamide, which exists in a zwitter-ion form. The causes of the observed increase in diffusion coefficient are the following.

1. The relative number of mobile ions in the polymer increases (as compared to the ions sorbed on the ionogenic groups).

2. The dielectric constant of the polymer increases with the concentration of the polar diffusant, leading to enhanced dissociation of the acid electrolyte and to generation of the more mobile ionic forms (protons).

3. The transfer of the acid from the amino to the amido sorption region shortens the distance between the positively charged groups of the polymer. This increases the probability of the "jump" of an anion from one positively charged group to the next through the non-polar medium provided by the weakly swelled polymer[86]. For example, keratin contains approximately 30 times more charged groups than Nylon-66, and as a result the self-diffusion coefficients in keratin are ~ 300 times greater than in Nylon. On the other hand uncharged molecules diffuse at comparable rates in these polymers, confirming the important role of electrostatic interactions in the polymer.

In the case of sulphuric acid the increase of the diffusion coefficient with concentration is due to the greater mobility of the hydrogen sulphate as compared with the sulphate ion[85]. It is assumed that the ratio of the first and the second dissociation constant of sulphuric acid is the same in the polymer as in the solution.

Table 3. Self-diffusion coefficients ($D$, $cm^2\ s^{-1}$) of ions and of alcohols in polyamides[85].

| Diffusant | Polycaproamide | Poly(hexamethylene diamine) | Keratin |
|---|---|---|---|
| $H^+$ (free) | — | $3\cdot10^{-8}$ | $8\cdot10^{-6}$ |
| $H^+$ (bound) | — | $6\cdot10^{-13}$ | $1.2\cdot10^{-10}$ |
| $Br^-$ | — | $6\cdot10^{-11}$ | $2\cdot10^{-8}$ |
| $HSO_4^-$ | $1.1\cdot10^{-6}$ | $6.8\cdot10^{-10}$ | $2.2\cdot10^{-8}$ |
| $SO_4^{2-}$ | $1.9\cdot10^{-7}$ | $2.0\cdot10^{-13}$ | $10^{-11}$ |
| $CH_3OH$ | — | $1.0\cdot10^{-7}$ | $1.0\cdot10^{-7}$ |
| $C_2H_5OH$ | — | $6\cdot10^{-8}$ | $6\cdot10^{-8}$ |

The diffusion coefficients of the proton were calculated independently by the Nernst–Hartley equation[6], assuming that the mobility of the proton is determined by the concentration of free ions. The anomalously high mobility of the proton in the polymer (as compared with other ions, see Table 3) suggests a special transport mechanism, similar to the "relay" model[6].

## 4. Effect of Water on the Diffusion of Electrolytes

When considering the diffusion of aqueous solutions of electrolytes in polymers with a high affinity for water we must inquire into the extent to which the transport of the electrolyte is affected by the competing (or independent) transport of water, and also into any structural changes in the polymer under the influence of a solvent as specific as water.

Studies of the diffusion of pure water in polymers are discussed in a number of reviews[109–111], and the kinetics and mechanisms of the sorption and diffusion of water in polymers are examined in detail. We shall only be concerned with those features of the transport of water which influence the mechanism of diffusion of electrolytes in polymers.

In the absence of capillary flow we have to consider two types of water transport: a) the diffusion mechanism, in which the driving force is a concentration gradient, and b) the viscous flow of water, in which the driving force is a difference in hydrostatic pressure between the two sides of the membrane. The relationship between the hydraulic ($G$) and the diffusional ($\bar{P}$) permeability is given by the dimensionless coefficient $w$ according to the equation[112]

$$w = GRT/\bar{P}\bar{V}_{H_2O}, \qquad (27)$$

where $\bar{V}_{H_2O}$ is the molar volume of water. The parameter $w$ is unity for the diffusion mechanism, and increases as we move towards a viscous flow regime.[113]

We must identify the type of transport if we wish to interpret the kinetic results correctly and to arrive at valid conclusions on the interactions between the flows of water and of electrolyte in the polymer. In the diffusion mechanism this interaction is unlikely, but in the case of viscous flow of the solvent through a membrane we can expect interaction between the flows of the components of an aqueous solution of electrolyte[113]. Since most diffusion measurements are made without an excess hydrostatic pressure of solvent we can assume that diffusional transport is predominant (at least, in the case of moderately swelled polymers).

The absence of interaction between opposing flows of electrolyte and of water in a hydrophilic system (acetyl cellulose) has been demonstrated[114] by comparing the forward and the reverse osmosis of sodium chloride solutions.

When discussing the ingress of an aqueous solution of electrolyte into a polymer we must consider the water content of the polymer matrix, since the specific state of the electrolyte (i.e. its dissociation and its hydration) are determined by it. Furthermore active absorption of water weakens the intermolecular interactions, increasing the mobility of the polymer segments and hence increasing the diffusion coefficients.

Another factor which must be considered when discussing the diffusion behaviour of electrolytes is the state of the water in the polymer. Three types of system can be formed by the interaction of the polymer with water: a) the water dissolves in the polymer with formation of a uniform, quasi-homogeneous medium, b) local groupings (clusters) are formed[109,115–117]), and c) the interaction results in filling of the macro-structural holes, pores, and capillaries (which may be either interconnected or isolated)[118,119].

Recent work by electrical conductivity and NMR methods (among others) has shown that macromolecular gels contain both free and quasicrystalline water[120]. The transition temperature of the latter form is below 0°C. In addition to these two forms we must also consider an intermediate form with its own distinct electrophysical and thermal properties[121,122].

The great variety of possible structural forms of the solvent in polymers makes it difficult to identify the mechanism of ion transport.

## 5. The Moving Electrolyte Boundary

The diffusion of electrolytes in hydrophilic polymers may involve, as was stated above, on the one hand specific interactions between the components of the diffusing

medium and the polymer and on the other hand interactions between the components themselves in the polymer matrix. Depending on which of these effects is predominant the motion of the electrolyte solution can occur as a single front or as a macroscopic distribution of flows. Experiment shows that the former situation is more typical of polymers in which the solubility of water is limited.

Fig. 5 shows the change in concentration of water and HCl in a film of ethyl cellulose during the diffusion of hydrochloric acid vapour. The concentration of water was determined gravimetrically, and that of HCl by a chemical desorption method and by a combustion method [123].

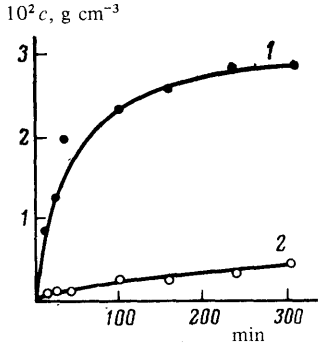



**Figure 5.** Kinetic curves for the sorption of $H_2O$ (*1*) and HCl (*2*) in ethyl cellulose [123].

The diffusion of electrolyte solutions in polymers very often gives rise to a sharp boundary between a region containing the electrolyte and a region in which no electrolyte is detected by the analytical method employed. The reasons for the formation of this sharp boundary have been discussed [124-126], and the following explanations have been suggested: a) a chemical reaction between the components of the diffusion system, and b) a sharp change in the structure of the polymer at the boundary between the swelled and the free zone.

The interaction between an acid and water has been shown [19] to produce a boundary of constant concentration of electrolyte whose motion is described by Eqn. (17) with

$$\lambda = [2D(c_0/c_x - 1)]^{1/2},$$

if the electrolyte and the solvent are diffusing as a single front, and

$$\lambda = (\pi D)^{1/2}(1 - c_x/c_0),$$

if the electrolyte and the solvent are diffusing at different rates as separate flows. For example, the diffusion of an aqueous solution of sulphuric acid in polycaproamide is typical of case a). The calculated value $D = (1.5 \pm 0.2) \times 10^{-9}$ cm$^2$ s$^{-1}$ is close to $D_{H_2O}$ in polycaproamide. The time for contact between the two oppositely moving fronts in diffusion from both sides has been used [127] to calculate diffusion coefficients. The motion of the boundary in the polymer in its most general formulation is discussed in Ref. 128.

## V. HYDROPHOBIC POLYMERS

One of the main characteristics of the transport of an electrolyte in hydrophobic polymers is the large difference in the rates of diffusion of different electrolytes. For example, the penetration of nitric acid through a Fluorlon-42 film 0.1 mm thick can be detected in 20–30 min, whereas over a year is needed with sulphuric acid [129]. In many cases the diffusion of electrolytes in these polymers is immeasurably slow.

We should note that permeability (as opposed to non-permeability) of a polymer by a particular electrolyte can usually be established with greater confidence. This is because the failure to observe permeation may be due to inadequate sensitivity of the method of detection or to insufficient time for diffusion. Evidently in this case it is better to characterise the permeability by the quantity $\bar{P}_{arb}$, calculated by the equation

$$\bar{P}_{arb} = c_{min} Vl/s\tau_0,$$

where $c_{min}$ is the minimum concentration of electrolyte which can be detected by the chosen analytical method, and $V$ is the extent of the medium in which transport is taking place through a film of thickness $l$ and working surface $s$ in time $\tau_0$. If no penetration is detected we can only state that the true permeability of the system is less than $\bar{P}_{arb}$.

**Table 4.** Diffusion coefficients of electrolytes in hydrophobic polymers ($c$ is the concentration of electrolyte in the aqueous solution).

| Polymer | Electrolyte | $c$, wt.% | Temp., °C | $D$, cm$^2$ s$^{-1}$ | Method of detection | References |
|---|---|---|---|---|---|---|
| Polyethylene | $HNO_3$ | 98 | 50 | $2.9 \cdot 10^{-7}$ | sorption | 134 |
| Polyethylene (NP) | HCl | 28—36 | 50 | $8 \cdot 10^{-7}$ | sorption | 135 |
| Polyethylene (NP) | NaCl | 1—10 | 20 | $(6-8) \cdot 10^{-11}$ | radio-isotope | 136 |
| Polyethylene (NP) | NaI | — | 24 | $2.2 \cdot 10^{-8}$ | radio-isotope | 137 |
| Teflon-4 | $HNO_3$ | 98 | 50 | $2 \cdot 10^{-9}$ | sorption | 134 |
| Teflon-4 | NaI | — | 24 | $9.6 \cdot 10^{-9}$ | radio-isotope | 137 |
| Teflon-4 | NaCl | 1—10 | 20 | $2-3 \cdot 10^{-11}$ | radio-isotope | 136 |
| Teflon-3 | $HNO_3$ | 98 | 50 | $7.7 \cdot 10^{-9}$ | sorption | 134 |
| Teflon-3 | NaI | — | 24 | $9.6 \cdot 10^{-9}$ | radio-isotope | 137 |
| Polystyrene | NaI | — | 24 | $25 \cdot 10^{-8}$ | radio-isotope | 137 |

The permeability of polymers to electrolytes has been compared with the volatility of the electrolytes [130-132], with the conclusion that the permeability of hydrophobic polymers to involatile electrolytes is at least three orders of magnitude lower than their permeability to volatile electrolytes. The low diffusivity of involatile electrolytes is ascribed to negligible sorption of these electrolytes in polymers. This classification into volatile and involatile electrolytes is useful in qualitative predictions of the permeability of polymers towards specified electrolytes by using only generally available tabulations. After studying the transport of electrolytes in polyester resins Alt [133] classifies electrolytes as "strongly diffusing" (HCl, HF, $HNO_3$, $H_2SO_4$), "weakly diffusing", and "involatile". We must stress the arbitrariness of the distinction between "volatile" and "involatile" electrolytes. For example, the permeation of sulphuric acid through Fluorlon is easily detected at high temperatures and concentrations, when the vapour pressure of sulphuric acid is only a few thousandths of a mmHg.

Many measurements of the diffusion coefficient $D$ in polymers have been reported, but in most cases the method used was inadequate[50]. Some results obtained by acceptable methods (see Chapter III) are listed in Table 4. We note the following facts. The diffusion coefficients of NaI in all the polymers examined are similar ($\sim 10^{-8}$ cm$^2$ s$^{-1}$), and almost three orders of magnitude higher than the diffusion coefficient of NaCl, although the molecular weight of NaI is almost twice that of NaCl. Obviously, the $D$ value for sodium iodide is anomalously large: this may be due to reduction of the iodide ion to $I_2$.[138] The diffusion coefficients of HCl and $HNO_3$ in polyethylene are similar, and their relative values are consistent with expectations from the molecular weights of the two acids. They are of the same order of magnitude as the diffusion coefficient of benzene in polyethylene (at "zero" concentration) $1.32 \times 10^{-7}$ cm$^2$ s$^{-1}$.[17] The diffusion coefficient of NaCl is several orders lower than the diffusion coefficients of HCl and $HNO_3$. No explanation of this fact has so far been offered.

### 1. Effect of the Concentration of Electrolyte in the External Solution on the Transport Parameters

The effect of the concentration of electrolyte in the external solution on the diffusion coefficients in the polymers presents a difficult problem. For example, in the polyethylene–$HNO_3$ system the $D$ value decreases by a factor of 1.5 when the concentration of the acid is increased from 45 to 60%.[134] However these results are not very reliable, because they were obtained from kinetic data on the change in weight of samples immersed in aqueous solutions and they do not describe the diffusion of the acid itself. An analysis[139] of kinetic sorption curves gave very complex results. Evidently, the Johnston equation (which can be used to calculate $D$ for a one-component diffusant) is not directly applicable to these systems.

The $D$ value for nitric acid in polyethylene was found[140,141] to increase from $3.2 \times 10^{-10}$ to $9 \times 10^{-10}$ cm$^2$s$^{-1}$ as the concentration of the acid in the external solution changed from 7 to 80%. It was determined by measuring (as a function of time) the electrical conductivity of a membrane in contact with the acid solution. These results are three orders of magnitude lower than the more reliable results reported in Refs. 134 and 142. The discrepancy probably arises from the failure to detect the diffusion of neutral particles in the electrical conductivity method.

The diffusion coefficients of HCl and $H_2SO_4$ in films of the KhSL lacquer (based on a perchlorovinyl resin) have been measured[27] as a function of concentration of the acid solution. At 60°C the coefficient $D_{HCl}$ increases from $3 \times 10^{-9}$ to $7.5 \times 10^{-9}$ cm$^2$ s$^{-1}$ as the acid concentration increases from 25 to 30%, and $D_{H_2SO_4}$ increases from $4 \times 10^{-10}$ to $19 \times 10^{-10}$ cm$^2$ s$^{-1}$ as the concentration increases from 50 to 90%. The authors ascribe the concentration dependence of $D$ to the transport of particles of different kind and different size from solutions of different concentration.

We have studied[135] the concentration dependence of $D_{HCl}$ in polyethylene. The diffusion coefficients were determined by the method of Dienes and Barrer, and they were also calculated by the formulae

$$\bar{D} = \bar{P}[c\rho]^{-1}, \tag{28}$$

$$D = \frac{1}{\rho}\frac{d\bar{P}}{dc}, \tag{29}$$

where $\rho$ is the density of the polymer and $c$ is the concentration of HCl in the polymer. For comparison we also measured $D$ for dry HCl at different partial pressures. We found that $\bar{D}$ increases with the concentration of the acid, approaching the value for dry HCl. The latter is independent of the partial pressure of HCl. The differential diffusion coefficient was found to be independent of the concentration of hydrochloric acid and equal to $D$ for dry HCl. These observations were explained and quantitatively described by postulating the presence of "free" HCl and "hydrated" HCl in the polymer[135].

It was also assumed that the hydrated molecules are practically immobile and do not contribute to the transport process. The conclusion was that under steady-state conditions $D_{HCl}$ does not depend on the concentration of hydrochloric acid. On the other hand under non-stationary conditions the effective diffusion coefficient varies because some of the diffusing molecules of acid are bound in hydrates, and therefore the integral diffusion coefficient $\bar{D}$ depends on the concentration of water in the polymer. The following equations for the concentration dependence were obtained:

$$\begin{aligned} \bar{D} &= D_0\gamma, \\ \bar{D} &= D_0(1 + MK\sigma^n_{H_2O}h^n_{H_2O})^{-1}, \end{aligned} \tag{30}$$

$$D = D_0\left[1 + \frac{6n(Kc_{H_2O})^{n-1}}{[(n-1)+2][(n-1)+3]} + \frac{6(Kc_{H_2O})^n}{(n+2)(n+3)}\right]^{-1}, \tag{31}$$

where $\gamma$ is the activity coefficient of HCl in the polymer, defined as the ratio of the concentration of "free" molecules to the total concentration of HCl in the polymer, $D_0$ is the diffusion coefficient of the free HCl molecules, $c_{H_2O}$ is the concentration of "free" water molecules in the polymer, and the other symbols are defined above. From the $\bar{D}$ values determined by the method of Dienes and Barrer, together with Eqn. (31), we found the value of $n$ (the number of $H_2O$ molecules associated with one hydrated HCl molecule) to be $4.13 \pm 1.69$, which can be compared with the value obtained from sorption measurements[129-131] ($n = 5.01 \pm 1.28$). Thus consistent values of $n$ were obtained in independent series of experiments, giving indirect confirmation of the validity of our postulate of hydrate formation. We should stress that these results were obtained for a single "polymer–acid" system, over a restricted range of HCl concentrations (28–34%), and at a single temperature (50°C), and therefore the problem of the dependence of the number of molecules in the hydrate upon the nature of the polymer and of the acid, the concentration of the acid, and temperature is still unsolved.

A rapid increase in the permeability of polymers with concentration of the electrolyte solution has been reported[130,143]. It is pointed out[131] that this rapid growth can be explained by assuming proportionality between the permeability and the vapour pressure of the electrolyte above its aqueous solution (which increases very rapidly with concentration). The concentration dependence of the permeability of films towards volatile electrolytes is accurately described by the expression

$$\bar{P} = \bar{P}_0 h, \tag{32}$$

where $\bar{P}_0$ is the permeability constant, independent of the concentration of electrolyte in the external solution, and $h$ is the vapour pressure of the electrolyte over the aqueous solution[132,144]. Eqn. (32) was tested by studying the permeability of films to HCl, HF, and $HNO_3$.

## 2. Effect of the Nature of the Polymer on the Transport Parameters

Experimental data on the effect of the nature of the polymer on the diffusion coefficients of electrolytes are very few. We see from Table 4 that $D_{HNO_3}$ in polyethylene is much greater than the diffusion coefficients in Fluorlons. This is consistent with the conclusion that gases have relatively low diffusion coefficients and relatively high solubilities in fluorine-containing polymers [145]. However in the case of the involatile electrolyte NaCl the diffusion coefficients in polyethylene and in Teflon are very similar. This may be due to differences in the diffusion mechanisms of $HNO_3$ and NaCl. Indirect information on the effect of the nature of the polymer on the diffusion coefficients of electrolytes in the polymer can be obtained from data on the permeation constants [Eqn. (17)].

The permeation coefficient is a function not only of the diffusion coefficient but also of the concentration of electrolyte solution in the surrounding medium. Sometimes it is also a function of the chosen method of detection [146]. Therefore it is important to ensure that when permeation coefficients are compared they are obtained under identical external conditions. The functional relationship between the permeation coefficient and the diffusion coefficient (and other factors) is not known in general. The following empirical relation applies to some systems [147]

$$\lambda_0 = A_0 h_a^b, \qquad (33)$$

where $\lambda$ is the permeation coefficient, $A_0$ and $b$ are empirical constants, and $h_a$ is the vapour pressure of acid over the solution. For many polymer–electrolyte systems $D$ can be evaluated from data on the concentration dependence of permeation coefficients [65].

The diffusion coefficients of NaOH, HCl, and $H_2SO_4$ in Pentaplast (3,3-bis(chloromethyl)oxacyclobutane polymer) have been measured [148]. At 40°C they are $1.4 \times 10^{-5}$, $0.4 \times 10^{-5}$, and $1.7 \times 10^{-5}$ cm$^2$ s$^{-1}$ respectively (radiometric method). These values are surprisingly high: thus, $D_{HCl}$ in NP polyethylene, a material in which diffusion coefficients are relatively high, is only $8 \times 10^{-7}$ cm$^2$ s$^{-1}$. These high values of $D$ are all the more remarkable in view of the low values of the permeability constant and of the permeation constant of HCl in Pentaplast in comparison with other polymers [149]. Equally surprising are the unusual dependences of the diffusion coefficients for volatile and for involatile electrolytes for water and nitric acid upon the logarithm of the permeation constants of these polymers for HCl. It follows that polymers can be classified according to their permeability towards electrolytes, as had been done previously for their permeability towards gases [150]. Fluorlon-3M has the lowest permeability of all the polymers examined. Within the Fluorlon series we note a clear correlation between the permeability for HCl and the permeabilities for $HNO_3$ and $H_2O$. The permeability for the latter diffusants is always much greater than that for HCl.

The introduction into hydrophobic polymers of polar substances or polar groups (carboxyl, carbonyl, or amino) invariably increases the permeability towards electrolytes, possibly as a result of increased sorption of the diffusant [142,151-153].

## 3. Effect of Temperature on Transport

The linearity of the plots of $\lg D$ against reciprocal temperature has been noted by many workers. The activation energies for diffusion $E_D$ were calculated from these plots: some of the reported $E_D$ values are listed in Table 5. Comparing these values with the activation energies for the diffusion of gases and vapours of similar molar volumes [17,50] we note that the former are somewhat lower. The cause of this phenomenon has not yet been analysed.

**Table 5.** Activation energy for the diffusion of electrolytes in polymers.

| Polymer | Electrolyte | $E_D$, kcal mole$^{-1}$ | Refs. |
|---|---|---|---|
| Poly(ethylene terephthalate) | $H_2SO_4$ (53%) | 12 | 177 |
| Poly(vinyl chloride) (plasticised) | $HNO_3$ (60%) | 14 | 176 |
| Poly(vinyl chloride) | HCl | 3.3 | 176 |
| Teflon-4 | $HNO_3$ (98%) | 4.5 (>323 K)<br>12.1 (<323 K) | 134 |
| Polycarbonate | $HNO_3$ | 10 | 178 |
| Polyethylene | $HNO_3$ (98%) | 4.3 | 179 |

Linear relationships are found also between the logarithm of the permeability constant $\lambda$ and reciprocal temperature [147,154], but the physical significance of the "activation energies" calculated from these results has not been discussed.

The activation energy of the permeability has been determined [144] for HCl diffusing through polyethylene (PE), polystyrene, and poly(ethylene terephthalate): 8.5, 4.3, and 10 kcal mole$^{-1}$ respectively. These values are typical of activated diffusion processes.

## 4. Views on the Transport Mechanism of Electrolytes in Hydrophobic Polymers

In the earlier work the permeation of electrolytes was treated as diffusion through interconnected pores (see, for example, Refs. 129, 155, and 156). However this model could not explain factors such as the high selectivity of the films, the concentration dependence of the permeability, and the high activation energies involved. A full analysis of the experimental information on the permeation of gases through polymer films has shown that in sufficiently thick films and at temperatures above $T_g$ the mechanism of transport is diffusion rather than motion through a system of pores [157]. Therefore most workers now believe that the transport of electrolytes through hydrophobic polymers also occurs by diffusion.

These views on the mechanism of transport in hydrophobic polymers do not take account of the defects which may be present in a particular sample (for example, thin films may contain pores extending across the whole thickness of the sample, which are absent in thicker films of the same material). Transport associated with the presence of micro-defects has been discussed in some recent papers [158,159]. In particular, defects can be produced in polyethylene films by irradiation with a mercury lamp [160].

Various views have been expressed on the nature of the diffusing particles. According to some, the diffusing species are individual ions (hydrated, or not hydrated). According to others the diffusing species are undissociated molecules freed from their hydration shell. The resolution of this problem is complicated by the failure of some workers to distinguish between particles present in the polymer and particles responsible for matter transport.

The polymer must contain some particles able to transport matter, but there is no justification for the assumption that all particles present in the polymer can contribute to the transport process.

Let us consider the validity of the assumption that electrolytes are transported as ions in hydrophobic polymers. The concentration of ions in these polymers is probably low: this follows both from general considerations of the dissociation of electrolytes in media of low dielectric constant [161] and from experimental data. Films in contact with solutions of electrolytes keep a high electrical resistance [132,162]. In contrast, the electrical resistance of a hydrophilic film of PK-4 polyamide decreases by 7 orders of magnitude in 20–40 min after immersion in a solution of ammonium hydroxide [132]. Calculation shows [132] that if the whole of the HCl sorbed by polyethylene from hydrochloric acid solution were in an ionic form the electrical conductivity of the film would be 10 orders of magnitude higher than the experimental value. (See also Refs. 163 and 164 on the formation of ion pairs in polymers.) The fact that polyethylene films in contact with electrolyte solutions have a higher conductivity than films with metallic contacts has been ascribed to the adsorption of ions on the film surface [165,166].

The active conductance of plasticised poly(vinyl chloride) (PVC) is found [167] to be increased by diffusion of HCl: even involatile acids such as phosphoric acid diffuse readily in plasticised PVC [168,169], possibly as a result of the "hydrophilisation" of PVC by the plasticiser. The increase in electrical conductivity of hydrophobic polymers resulting from the addition of polar plasticisers has been discussed [170] in terms of the increased mobility and concentration of the ions in the polymer. Another possible explanation of the change in conductivity and dielectric constant of the films is chemical interaction between the diffusing species and the film, analogous to that observed in the "polyethylene–nitric acid" system [167].

It has been pointed out [170,171] that the activation energy for conduction is much higher than the activation energy for the migration of small molecules in polymers, the values for polypropylene and polystyrene being 34.6 and 30 kcal mole$^{-1}$ respectively. These high activation energies for conduction are observed because they include contributions from the energy of the ionic "jump" (corresponding to the activation energy for molecular diffusion) and from the energy of formation of the ion (which is inversely proportional to the dielectric constant of the medium [172]). It has been suggested [170] that the ionic conductivity is determined mainly by ionisation under the influence of the electric field. In the presence of a sufficiently strong field the energy barrier is lowered and the conductivity increases as a result of the increased concentration of ions [173]. Thus the transport of electrolyte as ions in a hydrophobic polymer seems unlikely in the absence of an external electric field.

The hypothesis that transport occurs by undissociated molecules is supported by the following facts. The rate of transport of HCl through films of polyethylene, polystyrene, and poly(ethylene terephthalate), and of ammonia through polyethylene, does not depend on whether the electrolytes are diffusing from an aqueous solution or from the dry gas phase: in other words, the rate of transport under steady state is unaffected by the presence of water in the external phase [131,144]. Hence we conclude that the transport involves the same particles in both cases, and that these particles must be undissociated molecules free from their hydration shell since no other particles can be conceived in the case of diffusion from the dry gas. The lack of hydration shells around the diffusing molecules can be inferred also from the observed lack of dependence of the rate of transport of water from acid solution upon the nature of the acid. If the electrolyte were transported by hydrated particles we would expect the transport to be accompanied by varying amounts of water as a result of differences in the degree of hydration of different ions and of differences in the various flows. However it is found that for a given polymer the rate of transport of water is uniquely determined by the partial pressure of water vapour above the solution of acid [132,174].

In general [132,144] the transport of volatile electrolytes through films of hydrophobic polymers involves three steps: extraction of the electrolyte by the surface layer of the polymer, diffusion through the thickness of the polymer, and re-extraction on the far side of the film. Under steady-state conditions this process is analogous to the transport of gases, and is described by the equation

$$J = D(a_{1n} - a_{2n})/l \simeq Da_{1n}/l, \tag{34}$$

where $J$ is the flow through a film of thickness $l$, $D$ is the differential diffusion coefficient, and $a_{1n}$ and $a_{2n}$ are the activities of the electrolyte in the polymer on the near and the far side of the film respectively. The quantity $a_{1n}$ is related to the activity of the electrolyte in the external solution ($a_B$) by the expression

$$a_{1n} = Ka_B, \tag{35}$$

where $K$ is the thermodynamic distribution constant of the electrolyte between the polymer phase and the aqueous solution. Combining Eqns. (34) and (35) we obtain an equation for the permeability of the film as a function of the composition of the external solution, and of the properties of the diffusant and of the polymer:

$$J = DKa_B/l. \tag{36}$$

The product $DK$ is, effectively, the permeability constant $P_0$, which depends on the properties of the polymer and of the diffusant, and the effect of the composition of the external medium on the permeability is uniquely determined by the quantity $a_B$. The parameter $K$ is related to the standard change in free energy of extraction ($\Delta G^\circ_e$) by the equation

$$\Delta G^0_e = -RT \ln K. \tag{37}$$

The transfer of the electrolyte from the aqueous solution into the polymer can be described as the removal of the electrolyte from the aqueous solution (i.e. the reverse of dissolution) followed by the mixing of the electrolyte with the polymer:

$$\Delta G^0_e = -\Delta G^0_{sol} + \Delta G^0_m, \tag{38}$$

where $\Delta G^\circ_{sol}$ is the standard change in free energy accompanying the formation of an aqueous solution at infinite dilution, and $\Delta G^\circ_m$ is the standard free energy change on mixing the electrolyte and the polymer. Tentative calculations for acids have shown [132] that the main contribution to $\Delta G_e$ comes from the term $(-\Delta G^\circ_{sol})$, i.e. the energy needed to remove the electrolyte from the aqueous solution is determined mainly by the distribution constant. However differences in extractability are themselves related to differences in the $\Delta G^\circ_m$ value, which is directly related to the amount of sorption by the expression

$$\Delta G^0_m = -RT \ln \varphi_1. \tag{39}$$

The quantity $\varphi_1$, i.e. the volume fraction of solute, can be calculated to a first approximation by using the Flory equation[175] in the simplified form

$$-\ln\varphi_1 = 1 + \bar{V}_1(\delta_1 - \delta_2)^2/RT, \qquad (40)$$

where $\bar{V}_1$ and $\delta_1$ are the molar volume of the solute and its solubility parameter respectively, and $\delta_2$ is the solubility parameter of the polymer. There is indirect evidence (weak concentration dependence of the permeability, similarity of the diffusion coefficients in different polymers) that Eqn. (36) does not apply in real systems.

The nature of the polymer, its affinity towards water molecules, and the concentration of water (which affects the physicochemical properties of the polymer) have a strong influence on the type and on the mechanism of the transport of electrolytes in polymer systems.

The diffusion of electrolyte solutions in hydrophilic polymers, in which the solubility of water is high, is characterised by equilibrium parameters (such as the dissociation constant and the diffusion parameters $D$, $\lambda_0$, and $u_i$) close to the values of the same parameters for solutions. The decrease in mobility of molecules and ions in a polymer (as compared to their mobility in solution) is due to the increased length of the diffusion path and to interactions between the diffusing particles and the polymer. In hydrophilic polymers with a limited water solubility the dissolved water cannot form a continuous aqueous environment within the polymer matrix, and the diffusion of ions occurs by activated jumps between polar groups, resulting in a $D$ value much lower than in the solution.

The diffusion of electrolytes in hydrophobic polymers is similar (in general) to the diffusion of gases and vapours which are inert towards the polymer, but the interaction of water with the polymer has a substantial effect on the diffusion process during the initial non-stationary period.

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