Conditions for Enhanced Chemical Diffusion of Ions in Polymers. A Review

Robert A. Huggins*[1] and John M. Huggins[2]

Department of Materials Science and Engineering, Stanford University, Stanford, California 94305, and the Department of Chemistry, California Institute of Technology, Pasadena, California 91125. *Received July 11, 1977*

ABSTRACT: Basic relations involved in the concurrent diffusion of several species in solids are presented, with emphasis on conditions which can produce very large chemical diffusion coefficients in composition gradients. In extreme cases, interaction between ionic and electronic fluxes can lead to values which greatly exceed those found in common liquids. Especially large enhancement can occur in materials in which the concentration of mobile ions is much greater than that of conducing electrons or holes, but in which charge is transported predominantly by electronic species, due to their greater mobility. Polymers designed to emphasize such characteristics should have a number of important potential applications.

For some time there has been a considerable interest in the design of polymeric structures containing interconnected voids such that they allow the selective permeation of specific molecules. Such polymeric materials are currently being used for such applications as dialysis membranes in artificial kidneys, for water purification, and for the local delivery of medically active species at controlled rates in both humans and animals.

Ionic transport in polymers is also being used for a number of applications, including ion exchange materials and solid electrolytes for use in fuel cells, or, perhaps, batteries. An important requirement of the polymer in the latter case is that it be an electronic insulator. That is, that charge transport occurs primarily by the motion of ionic species through the structure.

In addition, there has been a good deal of work on electronic transport in semiconducting polymers, and photoconducting polymeric solids are an important component of at least one of the current commercial copying machines.

A considerable amount of interest has been generated recently, among both chemists and physicists, in polymeric solids which are very good electronic conductors, with special interest being given to those in which the charge transport is essentially unidirectional.[3a] Some of these one-dimensional electronic conductors, such as the organic charge-transfer salts of TCNQ,[3b-10] $(SN)_x$,[11] and a number of materials containing linear arrangements of transition metal complexes[12,13] have been found to have quite unusual electronic and optical properties. Superconductivity has even been found, albeit at very low temperatures, in polymeric $(SN)_x$.[14]

In the last few years the recognition of the possibility of a number of practical applications has focused attention upon inorganic materials which exhibit appreciable amounts of mixed ionic and electronic conductivity.[15-17] Of particular interest are materials in which solute species (e.g., alkali metal ions or very electronegative anions) can be "inserted" into the van der Waal's space between covalently bonded or metallically bonded structural constituents. One example is the intercalation of alkali metal ions into the layer structure of transition-metal chalcogenides. Recognition of this possibility[16,18,19] has led to efforts aimed at the development of an interesting new type of high specific energy battery based upon the Li/Li_xTiS_2 electrochemical cell.[20,21]

While most of the attention that has been given to such phenomena to date has involved crystalline inorganic solids, many of the important features of this type of behavior are quite general and should be applicable to a wide range of materials, including many potential polymers. Examples of such polymeric mixed conductors are the charge-transfer complexes of poly(2-vinylpyridine)–iodine and poly(2-vinylquinoline)–iodine which are attractive as cathodes in a Li/I_2 primary cell made for use in implantable cardiac pacemakers.[22,23] In addition, it has been found that cationic and anionic species can be diffused into and out of some of the one-dimensional inorganic polymers which are currently being investigated primarily because of their unusual electronic behavior. There have also been reports[24] of the use of ion-radical salts based upon TCNQ as ion-selective electrodes due to their combination of ionic and electronic transport.

One of the important aspects of mixed ionic–electronic conductivity is that the interaction of these two charge fluxes can result in a large enhancement of the rate of ionic diffusion if a concentration gradient is present. This can lead to unusually large values of the chemical diffusion coefficient in some cases. For example, a chemical diffusion coefficient $\tilde{D}$ of 0.47 $cm^2\ s^{-1}$ has been measured in Ag_2S at 200 °C,[25] and $\tilde{D}$ has been found to be about 2.5×10^{-4} $cm^2\ s^{-1}$ at 380 °C in Li_3Bi.[26] For comparison, diffusion coefficients in simple liquids are generally in the range $1–10 \times 10^{-5}$ $cm^2\ s^{-1}$. Thus we see that much greater values of ionic transport can sometimes be attained in solids than in liquids.

The purpose of this paper is to present the basic relations involved in the concurrent diffusion of several mobile species in solids in which a composition gradient is present, giving particular attention to cases in which both ionic and electronic species are mobile. The critical features and parameters that lead to unusually fast chemical diffusion will become evident. It is hoped that such information may be of use to those concerned with the design and synthesis of new polymeric materials with special properties.

Basic Relations Concerning The Transport of Species in the Presence of a Composition Gradient

When a gradient in composition is present within a solid (or liquid) the transport parameters of the various mobile species are interrelated. The macroscopically observable quantity which is generally used to describe the complex transport process tending toward compositional equilibration under such conditions is the chemical diffusion coefficient, $\tilde{D}$. General equations have been presented recently for its microscopic description and its relation to other kinetic parameters in solids,[27] and this general approach will be followed here, in order to show which factors control the kinetics of chemical diffusion under various circumstances. It will be seen that the compositional dependence of certain thermodynamic parameters can lead to a large enhancement in ionic transport and thus may be of special importance in certain circumstances.

In this approach, particle fluxes are expressed in terms of the individual kinetic and thermodynamic properties of the

different ionic and electronic species present in the solid. Effects resulting from volume changes and macroscopic flow will not be considered. The sublattice of one component is used as the frame of reference for the motion of all the other species, and it will be assumed that the diffusion length is small compared to the dimensions of the whole system.

In general, in an isothermal system and if Onsager's cross-efficients are negligible, the flux density of species i (in particles/cm^2 s) under the influence of a gradient in the electrochemical potential η_i (related to one particle) is given in the one-dimensional case by

$$j_i = -\frac{\sigma_i}{z_i^2 q^2}\frac{\partial \eta_i}{\partial x} \tag{1}$$

where σ_i, z_i, and q are the partial electrical conductivity due to the transport of species i, the charge number (effective valence) of i, and the elementary charge, respectively. The electrical conductivity σ_i may be replaced by an expression including the product of the concentration c_i and the electrical mobility u_i (mean particle drift velocity per unit field) or, alternatively, the general mobility b_i (mean particle drift velocity per unit force), where $b_i = u_i/|z_i|q$,

$$\sigma_i = |z_i|qc_iu_i = z_i^2q^2c_ib_i \tag{2}$$

Also, the electrochemical potential η_i may be divided into two terms, one containing the chemical potential μ_i (per particle) or the activity a_i and the other the local electrostatic potential ϕ within the solid

$$\eta_i = \mu_i + z_iq\phi = \mu_i^0 + kT \ln a_i + z_iq\phi \tag{3}$$

Here μ_i^0, k, and T are the chemical potential of species i in the standard state ($a_i = 1$), Boltzmann's constant, and the absolute temperature, respectively. Inserting eq 2 and 3 in eq 1 yields for the particle flux density of the component i

$$j_i = -\frac{kTu_i}{|z_i|q}\left[\frac{\partial \ln a_i}{\partial \ln c_i}\frac{\partial c_i}{\partial x} + \frac{z_iqc_i}{kT}\frac{\partial \phi}{\phi x}\right] \tag{4}$$

The factor before the bracket has the dimensions of a diffusion coefficient and is the component diffusion coefficient D_i, often called the self-diffusion coefficient. According to eq 2 it can be written as

$$D_i = kTu_i/|z_i|q = b_ikT \tag{5}$$

This quantity is thus simply proportional to the mobility of the species in question and is a measure of the microscopic random motion of the particles of species i in the crystal in the absence of a concentration gradient. The self-diffusion coefficient obeys the Nernst–Einstein equation regardless of whether the solid solution is thermodynamically ideal or nonideal and is the diffusion coefficient which is directly measured in the case of ideal dilute solutions of neutral species. It is also often evaluated by the use of radioactive tracers in otherwise homogeneous materials and is related to the (radio) tracer diffusion coefficient D_{T_i} by $D_{T_i} = f_iD_i$, where f_i is the correlation factor.

The inner electric field $\partial\phi/\partial x$, which cannot be experimentally determined, may be eliminated from eq 4 by the condition that, except for transient conditions involving the accumulation of a significant local space charge, charge flux balance must be maintained. That is, for all species, if there is no externally applied electric potential difference,

$$\sum_i z_ij_i = 0 \tag{6}$$

Inserting eq 4 in eq 6 and solving for $\partial\phi/\partial x$ and then using this expression in eq 4 yields the flux denisty for species i in terms of transport parameters and activity gradients related to it and to all other ionic and electronic species j

$$j_i = -D_i\left[\frac{\partial \ln a_i}{\partial \ln c_i} - \sum_j t_j\frac{z_i\,\partial \ln a_j}{z_j\,\partial \ln c_i}\right]\frac{\partial c_i}{\partial x} \tag{7a}$$

$$= -D_i\left[(1-t_i)\frac{\partial \ln a_i}{\partial \ln c_i} - \sum_{j\neq i} t_j\frac{z_i\,\partial \ln a_j}{z_j\,\partial \ln c_i}\right]\frac{\partial c_i}{\partial x} \tag{7b}$$

The symbol $t_i = \sigma_i/\Sigma_j\sigma_j$ is the transference number for species i.

As a result of the ionization equilibrium, in which the activities of neutral species are related to those of their ionic and electronic constituents within solids, we have

$$\mathrm{d} \ln a_i + z_i \mathrm{d} \ln a_e = \mathrm{d} \ln a_i - z_i \mathrm{d} \ln a_h = \mathrm{d} \ln a_i^* \tag{8}$$

where e, h, and i* represent electrons, holes, and neutral i species, respectively. Equation 7 may now be transformed into an expression containing only the (experimentally more relevant) activities and concentrations of neutral atomic species,

$$j_i = -D_i\left[\frac{\partial \ln a_i^*}{\partial \ln c_i^*} - \sum_{j\neq e,h} t_j\frac{z_i\,\partial \ln a_j^*}{z_j\,\partial \ln c_i^*}\right]\frac{\partial c_i}{\partial x} \tag{9a}$$

$$= -D_i\left[(1-t_i)\frac{\partial \ln a_i^*}{\partial \ln c_i^*} - \sum_{j\neq i,e,h} t_j\frac{z_i\,\partial \ln a_j^*}{z_j\,\partial \ln c_i^*}\right]\frac{\partial c_i}{\partial x} \tag{9b}$$

These equations give the flux density for any chemical component and hold both for the ionic species within the solid and for the macroscopically observable effective flux density of such species in their neutral form. These equations are distinct from those which were presented earlier (eq 7), however, as here the activity and concentration terms only involve neutral chemical species and neither electrons nor holes.

These general equations have a form similar to the familiar Fick's first law

$$j_i = -\tilde{D}_i\,(\partial c_i/\partial x) \tag{10}$$

where $\tilde{D}_i$ is the chemical diffusion coefficient for species i and

$$\tilde{D}_i = D_iW \tag{11}$$

The factor W is an "enhancement factor", defined by the quantity in the square brackets in eq 9b

$$W = \left[(1-t_i)\frac{\partial \ln a_i^*}{\partial \ln c_i^*} - \sum_{j\neq i,e,h} t_j\frac{z_i\,\partial \ln a_j^*}{z_j\,\partial \ln c_j^*}\right] \tag{12}$$

which causes the effective diffusion coefficient to be greater in the presence of a concentration gradient than it is in a chemically homogeneous material. This effect can be interpreted in terms of the influence of the transport of charged species upon each other, as first pointed out by Wagner.[28]

Chemical Diffusion in which Only Two Species are Mobile

In many cases this situation is simplified by the fact that two types of species (either two different ionic species, or one ionic and one electronic species) dominate the transport phenomena within the solid. When this is true, the chemical diffusion coefficients of the two species must be equal, and we can use the symbol $\tilde{D}$ for both.[29]

For the common and important case in which only one ionic and one electronic species (of opposite charge) have to be considered, so that $t_e = 1 - t_i$, the enhancement factor becomes

$$W = t_e\frac{\partial \ln a_i^*}{\partial \ln c_i^*} \tag{13}$$

and

$$\tilde{D} = D_it_e\frac{\partial \ln a_i^*}{\partial \ln c_i^*} \tag{14}$$

Table I
Value of Enhancement Factor under Various Conditions (Cases with Only One Ionic Species and Electrons Mobile)

	Thermodynamic assumptions	Concn assumptions	Transference No. assumption	Enhancement factor W
(a)	General	General	General	$t_e\left[\frac{\partial \ln a_i}{\partial \ln c_i} + z_i\frac{\partial \ln a_e}{\partial \ln c_i}\right]$ or $t_e\left[\frac{\partial \ln a_i^*}{\partial \ln c_i^*}\right]$
(b)	General	General	$t_e << 1$	$<<\left[\frac{\partial \ln a_i^*}{\partial \ln c_i^*}\right]$
(c)	$\left[\begin{matrix}a_i \sim c_i \\ a_e \sim c_e\end{matrix}\right]$	General	General	$t_e[1 + z_i^2(c_i/c_e)]$ or $t_e[1 + (t_i/t_e)(D_{K_e}/D_{K_i})]$
(d)	$\left[\begin{matrix}a_i \sim c_i \\ a_e \sim c_e\end{matrix}\right]$	General	$t_i << 1$	$1 + z_i^2(c_i/c_e)$
(e)	$\left[\begin{matrix}a_i \sim c_i \\ a_e \sim c_e\end{matrix}\right]$	$c_i << c_e$	$t_i << 1$	1
(f)	$\left[\begin{matrix}a_i \sim c_i \\ a_e \sim c_e\end{matrix}\right]$	$\lvert z_i\rvert c_i = c_e$	$t_i << 1$	$1 + \lvert z_i\rvert$
(g)	$\left[\begin{matrix}a_i \sim c_i \\ a_e \sim c_e\end{matrix}\right]$	$c_i >> c_e$	$t_i << 1$	$z_i^2(c_i/c_e)$
(h)	$\left[\begin{matrix}\text{Ions general} \\ a_e \sim c_e\end{matrix}\right]$	General	$t_i << 1$	$t_e\left[\frac{\partial \ln a_i}{\partial \ln c_i} + z_i^2\left(\frac{c_i}{c_e}\right)\right]$

If the material is predominantly an electronic conductor, so that $t_e \to 1$, we have simply

$$W = \partial \ln a_i^*/\partial \ln c_i^* \tag{15}$$

and

$$\tilde{D} = D_i(\partial \ln a_i^*/\partial \ln c_i^*) \tag{16}$$

This is the case previously discussed by Wagner.[30] Using the definition of the activity coefficient $\gamma_i = a_i/c_i$, the enhancement factor under that situation can also be written in the form

$$W = \left[1 + \frac{\partial \ln \gamma_i}{\partial \ln c_i}\right] = \left[1 + c_i\frac{\partial \ln \gamma_i}{\partial c_i}\right] \tag{17}$$

as derived for metals by Darken.[31]

On the other hand, for predominantly ionic conductors, where the transference number of the ionic species is much larger than that for the electronic species, eq 13 can be rewritten as

$$W = \left(\frac{\sigma_e}{\sigma_i}\right)\frac{\partial \ln a_i^*}{\partial \ln c_i^*} \tag{18}$$

and by using eq 2 and 5, we get

$$W = \frac{c_e D_e}{z_i^2 c_i D_i}\frac{\partial \ln a_i^*}{\partial \ln c_i^*} \tag{19}$$

and then

$$\tilde{D} = \frac{c_e D_e}{z_i^2 c_i}\frac{\partial \ln a_i^*}{\partial \ln c_i^*} \tag{20}$$

Thus we see that, in this case, the chemical diffusion coefficient for the ionic species is dependent upon the component or self-diffusion coefficient of the electrons, not the ions.

Let us now further examine the value of the enhancement factor W under several different situations for the common and important case in which only one ionic species and one electronic species (assumed to be excess or mobile electrons) have to be considered, the transference numbers of all other species being negligible. From eq 7, 10, and 11, the enhancement factor for the ions can be written in terms of the properties of the charged ions and electrons as

$$W = t_e\left[\frac{\partial \ln a_i}{\partial \ln c_i} + z_i\frac{\partial \ln a_e}{\partial \ln c_i}\right] \tag{21}$$

since $t_e = 1 - t_i$ and $z_e = -1$.

For the special situation in which we can assume that both the ionic species and the electrons obey either Henry's or Raoult's law, i.e., γ_i and γ_e are constant, and in view of the electroneutrality condition

$$dc_e = z_i dc_i \tag{22}$$

from eq 21, we see that

$$W = t_e\left[1 + z_i^2\frac{c_i}{c_e}\right] \tag{23}$$

We can thus conclude that if $t_e \ll 1$, i.e., in the case of an electronic insulator with dilute mobile ionic species, W will tend toward zero, and the chemical diffusion of ions in response to a composition gradient will be very sluggish.

On the other hand, if electronic conduction predominates, $t_e \to 1$, and the value of W will depend sensitively upon the value of the ratio c_i/c_e. If $c_i \ll c_e$, W will approach unity, so the chemical diffusion coefficient for the ionic species becomes the same as the self-diffusion coefficient. If $z_i^2 c_i = c_e$, W becomes 2.

There are many interesting materials in which electronic conduction predominates ($t_i \ll 1$), and yet $c_i \gg c_e$. This is possible if the electrons have a much greater mobility than the ionic species, and it can lead to unusually large values of W, and thus of $\tilde{D}_i$, as pointed out by Wagner,[32] who cited a number of materials in which this has been found. Values of the enhancement factor as large as 70 000 have recently been found[26] in the intermetallic compound Li_3Sb.

Very large enchancement factors can also be present for

materials in which one can assume that only the electronic species exhibit ideal solution behavior. In that case eq 21 becomes

$$W = t_e \left[\frac{\partial \ln a_i}{\partial \ln c_i} + z_i^2 \frac{c_i}{c_e} \right] \quad (24)$$

The enhancement factor W is sometimes explained in terms of a microscopic model in which the more mobile species tend to move ahead of the others in a composition gradient. If they have different charges (or species of the same sign move at different rates in opposite directions) this creates an internal electric field in which the slower species are accelerated, and the faster ones are retarded, due to the requirement to maintain local charge flux neutrality.

It also should be pointed out that if the second term in either eq 23 or eq 24 is large enough, the temperature dependence of the chemical diffusion coefficient may be quite different from that of the component or tracer diffusion coefficients, due to the temperature dependence of c_i/c_e.

The values of the enhancement factor W that are expected under these various conditons are presented in Table I.

Discussion

It has been shown that one can get quite large values of the enhancement factor, which is the ratio of the chemical diffusion coefficient to the component or self-diffusion coefficient, under certain circumstances. In extreme cases, this can result in chemical diffusion coefficients in solids that are orders of magnitude greater than those found in liquids.

This has several important implications. One of these is that one may be greatly misled concerning the real value of the chemical diffusion coefficient if diffusion is evaluated by the use of nuclear magnetic resonance techniques, or by the common procedure of isotope exchange involving the use of radiotracers in chemically homogeneous systems, since both of these methods evaluate the component or self-diffusion coefficient, rather than the chemical diffusion coefficient. Further difficulties can also arise with the use of radiotracers in cases in which diffusion is microscopically very anisotropic, as is the case in some polymeric systems, as the correlation factor can have extreme values in such cases.

Chemical diffusion values can, of course, be obtained from component diffusion data if thermodynamic data are also at hand, so that the enhancement factor can be evaluated. While thermodynamic data are often not available, and may be difficult to obtain by traditional calorimetric methods, it has recently been demonstrated[33] that by use of appropriate electrochemical cells and coulometric titration techniques it is sometimes possible to get such information with both great precision and unusual compositional resolution. The chemical diffusion coefficient can also be directly measured by electrochemical methods in some cases by using a newly developed relatively simple galvanostatic intermittent titration technique[27] if the sample is a predominantly electronic conductor.

There are a number of potential applications for mixed ionic–electronic conductors with very high values of chemical diffusion coefficient. These include their possible use as solid solution electrodes in battery systems, highly active electrodes in fuel cells and ion pumps, catalysts, selective ion electrodes, electrochemical timers and memory elements, electrochromic display materials, etc.

As described in the preceding section, two conditions must coexist for maximum enhancement of ionic conductivity: a large concentration of mobile ions, and higher electronic than ionic conductivity. Polymeric materials show great promise for achieving these conditions. The concentration of free ions can be controlled through changes in the substituent pattern in the polymer structure, and with recent advances, a wide variety of electronically conducting polymers are becoming recognized. Therefore, it is certainly within reason to expect that a number of polymeric materials with the requisite combination of properties can be designed and synthesized.

The challenges presented in this paper and by the whole field of ionically, as well as electronically, conducting polymers make this an area in which considerable opportunity exists for the development of useful new materials.

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