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MACROMOLECULAR STRUCTURE AND SOLUTE DIFFUSION IN MEMBRANES: AN OVERVIEW OF RECENT THEORIES*

NIKOLAOS A PEPPAS† and DAVID L. MEADOWS††

School of Chemical Engineering, Purdue University, West Lafayette; Indiana 47907 (U.S.A.)

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Dedicated to Prof. Edward W Merrill of M.I.T. on the occasion of his 60th birthday.

Summary

An overview of macroscopic, mass transfer, irreversible thermodynamic and macromolecular theories is presented for application in solute diffusion through polymeric membranes Special emphasis is given to recent work on solute diffusion through microporous and non-porous membranes.

1. Introduction

There have been two major approaches that have emerged over the past several decades for the physical description of transport processes through polymer membranes. Accordingly, each theory has led to its own applications and its own ways of describing and modeling transport phenomena in membranes. There has also been evidence that shows the two approaches can be related.

The first approach for analysis of transport through polymer membranes is based on the generalized Fickian diffusion equations. The generalized equations are often referred to as Stefan—Maxwell equations. They have been most often applied to multicomponent gaseous diffusion processes [1], but can also be applied to liquid processes [2].

The second approach is based on the principles of irreversible thermodynamics. It employs phenomenological coefficients to correlate the gradients that exist across a membrane and their resulting fluxes. This approach has been applied to a wide range of problems, including desalination and wastewater treatment by reverse osmosis, ultrafiltration or microfiltration [3], biomedical and pharmaceutical engineering, [4], etc.

Although membranologists and engineers continue studying various ways of using these two theories to predict and explain experimental results in

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†To whom all correspondence should be addressed

††Present address Rohm & Haas Co., Bristol, PA 19007, U.S.A.

separation processes, polymer physicists have concentrated, especially in recent years, on a systematic investigation of molecular structural characteristics of polymeric membranes, which could be important in understanding solute diffusion [e.g. 3,5]. In fact, recent physical analyses have attempted to relate physical structure and diffusive properties for simple and complex polymeric systems. In this short review we attempt to summarize some of the important findings of recent work on this subject.

2. Theories of mass transport in membranes

2.1. Analysis of mass transport by multicomponent diffusion equations

Transport properties of gases and liquids are described by several theories which owe their development to classical and statistical mechanics. The accurate evaluation and practical application of transport coefficients have been possible for only very few systems. These systems are usually simple and contain monatomic molecules with binary collisions. The kinetic theory of dilute gases has been used to calculate the transport coefficients. An excellent summary of this analysis can be found in Chapters 7 and 8 of Hirschfelder et al. [6]. The entire development is based upon the Boltzmann integrodifferential equation for the distribution function $f(r,v,t)$. This equation has been solved for simple systems using various approximations. The most well known is the one offered by Chapman [7] which is based on the Enskog series analysis [8].

Analysis of complex systems including solutions and multicomponent systems is not possible with simple kinetic theories. Therefore, further analysis was developed for the study of transport phenomena in "dense" systems. A good summary can be found in Chapters 9 and 10 of Hirschfelder et al. [6].

2.1.1. Generalized Stefan—Maxwell equations

As a result of the analysis described above, a set of mathematical expressions may be used to describe the relation between fluxes and forces in multicomponent diffusion. The most general of these forms is referred to as the Stefan—Maxwell equations [1]. Numerous authors have derived different forms of the equations, although all derivations are fundamentally identical. The derivations are based on the solution of the Boltzmann equation with appropriate perturbations and the conservation equations. A preferred analysis of the Stefan—Maxwell equations can be found in the book by Chapman and Cowling [9].

The form of the Stefan—Maxwell equations used by Lightfoot [10], Cussler [11] and Krishna and Standart [2] is preferred in many investigations of membrane processes. This form of the equations is in general agreement with some of the classical contributions in the area of multicomponent diffusion such as the work of Stewart and Prober [12], Toor [13—15] and Cussler and Lightfoot [16, 17].

For a system of n independent components under isothermal conditions, diffusion of species i through the multicomponent system may be described by the Stefan—Maxwell equations, presented as eqns. (1)—(4), and henceforth designated the S—M equations,

$$\underset{\sim}{d}_i = \sum_{\substack{j=1 \\ j \neq k}}^{n} \frac{x_i x_j}{Đ_{ij}} (\underset{\sim}{v}_j - \underset{\sim}{v}_k) \,, \tag{1}$$

with

$$Đ_{ij} = Đ_{ji} \tag{2}$$

$$\sum_{i=1}^{n} \frac{x_i}{Đ_{ij}} = 0 \,. \tag{3}$$

$$\sum_{i=1}^{n} \underset{\sim}{d}_i = 0 \,. \tag{4}$$

In these equations subscript i designates the diffusing species and subscript j designates any one of all other components. Subscript k may be a reference component, although one may choose to use any other species without loss of generality. A common practice is to designate the component with the highest concentration as k (e.g. solvent for diffusion in solutions, or the membrane for diffusion through membranes). Also $\underset{\sim}{v}_j$ and $\underset{\sim}{v}_k$ are the velocities of components j and k respectively. The mole fractions of components i and j are designated x_i and x_j respectively, while the $Đ_{ij}$'s are the multicomponent diffusivities of the pairs ij. Finally, $\underset{\sim}{d}_i$ designates the generalized driving force for diffusion. For a system that has chemical potential, pressure, electrostatic potential and gravity gradients acting on it, $\underset{\sim}{d}_i$ may be written according to eqn. (5)

$$cRT\,\underset{\sim}{d}_i = c_i \underset{\sim}{\nabla}_{T,p}\ \mu_i + (c_i \overline{V}_i - \omega_i)\underset{\sim}{\nabla} p + (c_i \nu_i - \omega_i \sum_{k=1}^{n} c_k \nu_k) F \underset{\sim}{\nabla} \phi + \omega_i \sum_{k=1}^{n} \underset{\sim}{g}_k \,. \tag{5}$$

Here μ, p, ϕ and $\underset{\sim}{g}$ refer to the chemical potential, pressure, electrostatic potential and gravity forces, respectively; c_i, $\overline{V}_i$, ω_i and ν_i refer to the concentration, specific volume, mass fractions and ionic charge of solute (diffusing species), respectively; F is the Faraday constant, c is the total concentration of the system, R is the gas constant and T is the absolute temperature.

Equation (1) summarizes n—1 rate expressions known as the S—M equations and is a direct result of the solution of the Boltzmann equation with fluxes expressed in terms of velocities. However, contrary to other conventional diffusion expressions (such as the simplified Fickian diffusion expression), in eqn. (1) the forces are presented explicitly in terms of the fluxes.

The S—M relations cannot be used without the restraints expressed in eqns. (2)—(4). Equation (2) is a direct result of the symmetricity of the diffusion coefficient matrix. Equation (4) is a result of the use of the Gibbs—Duhem theorem. Equation (5) is an explicitly relation of the driving forces to all possible gradients that can be observed in the diffusion process.

Equation (1) must be recognized as the S—M relations for isothermal processes, because temperature effects have not been included in the expressions. Non-isothermal multicomponent diffusion may be described by eqn. (1′), where the additional term describes temperature gradients and includes the thermal diffusion coefficients, D^{T} [6].

$$\underset{\sim}{d}_i = \sum_{\substack{j=1 \\ j\neq k}}^{n} \frac{x_i x_j}{\text{Đ}_{ij}} (\underset{\sim}{v}_i - \underset{\sim}{v}_k) + \frac{\partial \ell n T}{\partial \underset{\sim}{r}} \sum_{\substack{j=1 \\ j\neq i}}^{n} \frac{x_i x_j}{\text{Đ}_{ij}} \left(\frac{D_j^{\mathrm{T}}}{c_j} - \frac{D_i^{\mathrm{T}}}{c_i} \right) . \qquad (1')$$

Several texts have simplified the S—M equations for the case of ideal thermodynamic systems where the only gradient is a concentration gradient. For example, Bird, Stewart and Lightfoot [18] simplified the S—M equations in the form of eqn. (6)

$$\underset{\sim}{\nabla} x_i = \sum_{\substack{j=1 \\ j\neq i}} \frac{x_i x_j}{c\mathcal{D}_{ij}} (\underset{\sim}{v}_j - \underset{\sim}{v}_k) . \qquad (6)$$

Apart from the use of mole fraction gradients instead of chemical potential gradients, the major difference between eqn. (6) and eqn. (1) is that the former is expressed in terms of the effective multicomponent diffusion coefficients, $\mathcal{D}_{ij}$. A very important characteristic of $\mathcal{D}_{ij}$ is that they are much more concentration dependent than the multicomponent diffusivities, Đ_{ij} of the more rigorous S—M relations [10, 11].

Because of the complex nature of S—M equations, many investigators have used simplifications of the S—M relations to describe their systems. The three simplifications that have appeared in the literature most often are generalized Fickian diffusion, Fickian diffusion and Nernst—Planck diffusion.

2.1.2. Generalized Fickian diffusion

The generalized Fickian diffusion equation may be described by eqn. (7)

$$\underset{\sim}{j}_i = \frac{c^2}{\rho} \sum_{j=1}^{n} M_i M_j \text{Đ}_{ij} \underset{\sim}{\nabla} x_{ij} \qquad (7)$$

Here ρ is the density, M_i and M_j are the molecular weights of component i and j respectively, and the other terms are as defined before. Equation (7), the generalized Fickian expressions (henceforth designated as GF relations), closely resemble the S—M equations except for the fact that in the GF equations the fluxes are explicit functions of the forces. This inversion from equation (6) to (7) can be done under conditions described elsewhere [6]. Actually, in the form written here, eqn. (7) includes only chemical potential gradients. Similar expressions can be written for the flux due to pressure gradients (pressure diffusion), the flux due to gravity gradients (forced diffusion) and the flux due to thermal gradients (thermal diffusion). The total fluxes due to these forces are the summation of all the individual fluxes [6].

2.1.3. Fickian diffusion

A further simplification of the GF relations for binary systems leads to the well known Fickian equation described by eqn. (8)

$$\underset{\sim}{j}_i = c\mathcal{D}_{ij}\underset{\sim}{\nabla} x_i \quad . \tag{8}$$

This equation is applicable to binary systems exhibiting thermodynamic ideality. The multicomponent diffusion coefficient, $Đ_{ij}$, used in the GF equations has now become the binary concentration-dependent diffusion coefficient, $\mathcal{D}_{ij}$.

2.1.4. Nernst—Planck analysis

The third important simplification of the S—M equations was developed by Nernst and Planck to analyze systems where the diffusion of one component is the important transport process and all the other components can be collectively called the "mixture". Therefore, the Nernst—Planck equations (henceforth designated N—P equations) apply to pseudobinary systems which are conveneintly described by eqn. (9):

$$\underset{\sim}{N}_i = -c\mathcal{D}_{\mathrm{im}}\,\underset{\sim}{d}_i + \frac{\sum\limits_{\substack{j=1\\ j\neq i}}^{n} \underset{\sim}{N}_j/Đ_{ij}}{\sum\limits_{\substack{j=1\\ j\neq i}}^{n} x_i/\;Đ_{ij}}\; x_i \tag{9}$$

Here $\underset{\sim}{N}$ designates molar flux with respect to a stationary coordinate system and the other terms are as defined before.

The diffusion coefficient appearing in the N—P equations, $\mathcal{D}_{\mathrm{im}}$, is the pseudobinary diffusion coefficient which is defined according to eqn. (9) in terms of the multicomponent diffusion coefficients, $Đ_{ij}$, as

$$\mathcal{D}_{\mathrm{im}} = \left[\sum_{\substack{j=1\\ j\neq i}}^{n} \frac{x_j}{Đ_{ij}}\right]^{-1} \tag{10}$$

The above description of the S—M equations and several useful simplifications was meant to be a brief overview. Several useful forms of the equations exist but are not discussed at this time. Many investigators have used the equations presented above to analyze a variety of transport processes. Some of the more important problems that have been solved using S—M concepts will now be presented.

2.2. Irreversible thermodynamics

In the last forty years the theory of irreversible thermodynamics has been vigorously developed and tested. The theory has been able to treat irreversible processes in a detailed macroscopic fashion, which was not possible with its classical forebear. Although the concepts of irreversible thermodynamics were known before the turn of the century, it was not until the statistical mechanical investigations of Onsager [19, 20] that the present macroscopic form of the equations appeared [21].

The theory of irreversible processes (henceforth designated as TIP) has been a partial answer to the questions raised by classical thermodynamics [22]. The development of TIP was inspired by the work of Onsager [19, 20] and expanded by Meixner [23, 24], Eckart [25], Prigogine [26] and De Groot [27] who developed modified expressions of TIP for thermal diffusion, thermoelectricity, viscous flow and heat transfer.

The dissipation function, $T\sigma'$, that is the product of temperature and entropy generation, was first recognized by Lord Rayleigh as early as 1873 [27]. Rayleigh recognized that the dissipation function calculated for any system is of the form,

$$T\sigma' = \sum_i J_i X_i \tag{11}$$

Here, the fluxes, J_i, are flows of matter, heat or electricity and the generalized forces, X_i, are gradients of temperature, chemical potential, electrical potential, etc.

Another relationship between J_i and X_i that has been known for many years is that in simple cases the forces and fluxes are linearly related to each other. Linear relationships were verified experimentally and are still consistent with the theoretical development of Onsager. For cases where there is more than one irreversible process occurring, each flux J_i is linearly related to all other forces in the summation of the expression for $T\sigma'$. The general form of the flux J_i is,

$$J_i = \sum_i L_{ij} X_i \tag{12}$$

where L_{ij} is the general linear coefficient or the phenomenological coefficients.

Meixner [24] pointed out that the flows or forces can be chosen arbitrarily to a certain extent. He established a set of requirements for determining the set of conjugate variables after one set of variables is chosen. The first rule is that the product of any flux and its conjugate force have the dimensions of entropy production. The second rule states that any transformation of fluxes and forces for a given system does not alter the sum of the products.

The choice of fluxes and forces in irreversible thermodynamics is similar to the choice of coordinate systems for the solution of problems in classical mechanics. The thermodynamic solution to an irreversible process produces useful correlations between observable phenomena only when the fluxes and forces correspond to those that lend themselves to experimental determination [28].

2.2.1. Onsager's theory

Onsager was the first to propose a relationship that would significantly advance the theory of irreversible thermodynamics. Onsager's principle may be stated as follows: for a system of n independent components, if J_i and X_i are chosen from the expression of $T\sigma'$ and are independent, the phenomenological coefficients L_{ij} of the linear laws satisfy the symmetric relation,

$$L_{ij} = L_{ji} \tag{13}$$

for all components i and j [19, 20]. Equation (13) is usually referred to as "the Onsager reciprocal relations".

Since the contributions of Onsager, TIP has been used by many investigators to describe processes in many different areas. For example, the application of TIP to ion-selective membranes [29—31] has helped to understand and quantify the phenomena of ion transport through a membrane. Another closely related application is electrolytic systems. TIP has been used to describe binary [32] and ternary systems [33]. There have been several investigations that applied TIP to transport through living membranes. Mammalian red blood cell membranes have often been used to obtain information about the passive properties that cell membranes exhibit when exposed to different solutes and solvents [34—36]. Kumar [37] tried to model complex living membranes by using ion-exchange membranes. Systems that have reactions taking place in the membrane have also been described using TIP [38].

In all of these examples, Onsager's reciprocal relations were used to test the data that were obtained. Inherent in this effort is the assumption that Onsager's theory is always true. Many investigators performed experiments to explicitly check which systems and system conditions verify Onsager's theory. This was essential because for many years it was known that the reciprocity relations and the linear laws become invalid when the system's forces deviated significantly from equilibrium.

A system that was initially expected to invalidate the rules of TIP was active transport. To model the process of active transport, investigators used a membrane system which coupled a chemical reaction and a vectorial flow caused by electric current [29, 40]. The system proved to be linear over the range of affinities that were studied.

A system that was proposed to be an invalidation of the Onsager theory was bulk flow across an open membrane [41]. The bulk flow was caused by an external pressure difference across the membrane, and the open membrane was completely nonselective to both the solute and solvent. Bresler and Wendt [41] concluded that reciprocity was not satisfied for their system. However, they did qualify their statement by stating that their conclusion could not be tested rigorously because of insufficient data on their system. Smit and Staverman [42] refuted their analysis by stating that the only condition under which reciprocity fails is "large forces and fluxes". Smit and Staverman went on to say that "the linear region (small forces and fluxes) is rather wide for most membranes and certainly it is the region which should be and is the subject of most studies on permeabilities of membranes".

Miller [21] prepared a review of the experimental data available on a variety of different irreversible phenomena. Thermoelectricity, electrokinetics, transference in electrolytic solutions, isothermal diffusion, heat conduction in anisotropic solids and thermogalvanomagnetic effects were all considered in detail. All the data did verify Onsager's reciprocal relations and TIP within experimental error.

More recent major efforts towards verification of these relations for membrane processes can be found in refs. [43—50].

2.2.2. Membrane permeability to nonelectrolytes: Kedem and Katchalsky development

The physical form of the forces and fluxes in eqn. (11) is very important for efficient use of these equations in engineering problems. The product of the forces and fluxes should be easily measurable. These criteria must also be fulfilled for all membrane systems.

The definition of the fluxes and forces commonly used for membranes was successfully done by Kedem and Katchalsky [51] in an analysis, henceforth referred to as the K—K theory. By analogy to eqn. (11) one can write eqn. (14), where the subscripts s and w refer to solute and solvent, respectively.

$$T\sigma = J_s\,\Delta\mu_s + J_w\,\Delta\mu_w\,. \tag{14}$$

The fluxes and forces defined in eqn. (14) may be transformed into simpler quantities. Chemical potentials can be related to the concentration and the applied hydrostatic pressure for an ideal solution. Concentration may in turn be transformed into osmotic pressure by van 't Hoff's law. An assumption in the K—K development is that of small concentration differences. The assumption allows the logarithmic average concentration to be approximated by the arithmetic average concentration. Finally, the solute and solvent fluxes may be related to the total volume flow and the diffusion flow. Consequently, phenomenological equations relating flows and forces defined by eqn. (12) take the form

$$\left.\begin{aligned} J_v &= L_p\Delta P + L_{pD}\Delta\pi \\ J_D &= L_{pD}\Delta P + L_D\Delta\pi \\ L_{pD} &= L_{DP}\,. \end{aligned}\right\} \tag{15}$$

Kedem and Katchalsky further simplified eqn. (13) by using the reflection coefficient defined by Staverman [52]

$$\sigma = -\frac{L_{\mathrm{pD}}}{L_{\mathrm{p}}} = \left[\frac{v_{\mathrm{w}} - v_{\mathrm{s}}}{v_{\mathrm{w}}}\right]_{\Delta\pi=0} \tag{16}$$

where v_{w} and v_{s} are the velocities of the solute and solvent, respectively. The reflection coefficient, σ, is an adequate measure of membrane selectivity and can be easily measured experimentally. As it is presently defined, L_{D} is still rather difficult to measure. An alternative approach is the use of the coefficient of solute permeability at zero volume flow, ω, which is defined as

$$\omega = \left[\frac{J_{\mathrm{s}}}{\Delta\pi}\right]_{J_{\mathrm{v}}=0} = \frac{\bar{c}_{\mathrm{s}}(L_{\mathrm{p}}L_{\mathrm{D}} - L_{\mathrm{pD}}{}^2)}{L_{\mathrm{p}}} \quad . \tag{17}$$

The parameters defined by Kedem and Katchalsky have important practical implications since L_{p}, σ and ω are easier to measure [53]. Indeed, the membrane science literature includes excellent experimental studies, too numerous to cite here, which have reported values of these parameters for different membranes, synthetic and biological.

Qualitative analysis of the effect of various structural properties of polymeric materials on the transport and diffusional behavior of solutes, including diffusivity, L_{p}, σ and ω has been available for many years [3, 53]. For example, we know that any transport barrier of the polymer (e.g. crystallinity, crosslinking, high concentration of polymer, etc.) leads to lower values of diffusivity and permeability. However, in recent years, there has been revived interest in the development of more accurate physical theories which could relate solute transport properties to the molecular structure of polymeric membranes.

3. Effects of polymer structure on solute diffusion

In this section recent research relating polymer structure to solute diffusion will be reviewed. Basic information about the physical theories which establish the dependence of the solute diffusion coefficient on the polymer structure will also be discussed.

3.1. Polymer structure and solute diffusion

Transport through membranes has been extensively reviewed in recent contributions which have appeared in the literature [3, 53]. In terms of applicability of theories of solution diffusion in membrane problems, several authors prefer to distinguish three types of polymeric membranes.

(i) Macroporous membranes: these are membranes with large pores, usually in the range of 0.1—1.0 μm. They are widely used in waste-water treatment and other industrial applications. Membranes with pores as small as 200 Å may be included in this category.

(ii) Microporous membranes: the pore size of these membranes ranges from 50 to 200 Å. The pores are slightly larger than the solute. Under these conditions the diffusion path of the solute through the pores may be restricted.

(iii) Non-porous (gel) membranes: as the term implies these are membranes that do not have a porous structure. The space between macromolecular chains (henceforth referrred to as the "mesh") is the only available area for diffusion of solutes. Molecular diffusion is the only mode of mass transport under concentration gradient only and convection is usually negligible. Non-porous membranes are of particular interest in novel laboratory separations of expensive specialty chemicals, including many newly developed genetically-engineered molecules.

Methods of preparing the various types of membranes mentioned above have been described in a monograph by Kesting [55].

3.2. Macro- and microporous membranes

Solute diffusion through porous membranes (macroporous and microporous) may be described by Fickian or multicomponent diffusion equations (see eqns. (1), (7), (8) and (9)). For diffusion through pores the diffusion coefficients refer to solute diffusion through the solvent-filled pores. The structure of the pores in the membrane is incorporated into the diffusion coefficient by means of the void fraction (porosity), ϵ, and the tortuosity, τ, of the membrane. When partition of the solute in the polymer can occur, a pore wall partition coefficient, K_p, must be incorporated into the diffusion coefficient. Thus, the final form of the diffusion coefficient is

$$\mathcal{D}_{\mathrm{eff}} = \mathcal{D}_{\mathrm{iw}} \frac{\epsilon K_{\mathrm{p}}}{\tau} \qquad (18)$$

where $\mathcal{D}_{\mathrm{iw}}$ is the diffusion coefficient of the solute through solvent, and $\mathcal{D}_{\mathrm{eff}}$ is the effective diffusion coefficient of the solute through the membrane.

In the special case of microporous systems where the size of the diffusing species is of the same order of magnitude as the diameter of the pore, special simplified expressions have been developed to describe the transport process. The Faxén theory [56] and the Quinn—Anderson theory [57] are most often used to describe the pore—solute diffusion process. Both theories are based on a hydrodynamic analysis of solute diffusion through porous systems in the absence of pressure gradients.

The general form of the Faxén equation [56], the earliest of a number of equations which relate normalized diffusion coefficients to solute size, is

$$\frac{\mathcal{D}_{\mathrm{im}}}{\mathcal{D}_{\mathrm{iw}}} = (1-\lambda)^2 (1 - 2.104\lambda + 2.09\lambda^3 - 0.95\lambda^5) \qquad (19)$$

where

$$\lambda = \frac{r_{\mathrm{s}}}{r_{\mathrm{p}}} . \qquad (20)$$

$\mathcal{D}_{\mathrm{im}}$ and $\mathcal{D}_{\mathrm{iw}}$ are the diffusion coefficients of the solute in the polymer and in water, respectively. The radius of the solute is represented by r_s, while the radius of the pore is represented by r_p.

For microporous systems it is also useful to employ an alternative definition of the solute effective diffusivity, $\mathcal{D}_{\mathrm{eff}}$, as

$$\mathcal{D}_{\mathrm{eff}} = \mathcal{D}_{\mathrm{iw}} \frac{\epsilon K_p K_r}{\tau} \tag{21}$$

where the parameter K_r of eqn. (21) depends upon the value of λ ($= r_s/r_p$), the ratio of molecular diameter to pore diameter. Satterfield et al. [58] studied restricted diffusion using a variety of binary systems of hydrocarbons and aqueous solutions of salts and sugars in silica—alumina catalyst beads, for which λ ranged from 0.1 to 0.5. For solutes that did not preferentially adsorb on the catalyst, their results were well correlated by

$$\log \left[\frac{\tau \mathcal{D}_{\mathrm{eff}}}{\mathcal{D}_{\mathrm{iw}}} \right] = -2.0\lambda \tag{22}$$

In a later study [59] using macromolecules, Colton et al. found reasonable agreement between eqn. (22) and the effective diffusion coefficient of certain compact and relatively rigid proteins.

3.3. *Non-porous membranes*

Optimum design (or selection) of membranes for separation systems requires understanding of two types of problems, i.e., problems related to the structure and morphology of the polymeric material and problems related to the diffusion process per se. From a materials point of view, optimum diffusive conditions can be achieved by controlling the crystalline phase, porous structure, degree of swelling, additive concentration, mesh size of the crosslinked macromolecular chains and thermodynamic transitions related to macromolecular relaxation phenomena, namely glassy/rubbery transitions in the presence of a solute and a swelling agent, usually water [60, 61]. From a diffusion point of view, thermodynamic interactions between the polymer and the diffusing species may be important. The nature of intensive variable gradients responsible for transport, such as chemical potential, pressure, electrostatic potential and temperature gradients must be investigated and controlled.

The solute partition coefficient, K_p, is largely a measure of solute preference for the polymer relative to the surrounding diffusion media. If the solute has a chemical structure similar to that of the polymer, the partition coefficient will be high, whereas if the structures are different, K_p will be low. Size-dependent steric effects can influence K_p.

The effect of the structure of polymers on the solute diffusion coefficient is more complex. For crosslinked or uncrosslinked rubbery polymers, Fickian diffusion is observed. The solute diffusion coefficient is dependent on the equilibrium polymer volume fraction in the swollen polymer matrix, the crosslinking density and the size of the solute. Recent theoretical analyses by Yasuda et al. [62, 63] and Peppas et al. [61, 64], give the general behavior of the solute diffusion coefficient, $\mathcal{D}_{\mathrm{im}}$, for highly swollen polymers.

$$\frac{\mathcal{D}_{\mathrm{im}}}{\mathcal{D}_{\mathrm{iw}}} = k_1 \left[\frac{\bar{M}_{\mathrm{c}} - \bar{M}_{\mathrm{c}}^*}{\bar{M}_{\mathrm{n}} - \bar{M}_{\mathrm{c}}^*}\right] \exp \left[-\frac{k_2 r_{\mathrm{s}}^2}{Q_{\mathrm{m}} - 1}\right] \tag{23}$$

Here $\mathcal{D}_{\mathrm{im}}$ and $\mathcal{D}_{\mathrm{iw}}$ are as previously defined, $\bar{M}_{\mathrm{c}}$ and $\bar{M}_{\mathrm{n}}$ are the number average molecular weights between crosslinks (for the network membrane) and before crosslinking (for the original polymer chains), respectively, $\bar{M}_{\mathrm{c}}^*$ is the value of $\bar{M}_{\mathrm{c}}$ below which no diffusion of the solute can occur, and r_{s} is the characteristic radius of the solute. The swelling ratio, Q_{m}, is expressed as v_2^{-1}, where v_2 is the polymer volume fraction in a completely swollen membrane. Finally, k_1 and k_2 are physical parameters characteristic of the polymer and the swelling agent.

It is evident from this analysis that the crosslinked structure of polymer membranes creates a "screening effect" on solute diffusion through polymers even for highly swollen systems. For uncrosslinked polymers, this "screening" is provided by the mesh formed by entangled chains, whereas in semicrystalline polymers the crystallites act as physical crosslinked. Models and new molecular theories for concentrated polymer solutions and networks, as well as for their screening effect on diffusion, have been recently discussed by deGennes [54] and Nyström and Roots [5].

The main mechanism of solute diffusion is through the water (solvent) regions of the membranes, as shown experimentally with a variety of polymers [65, 66]. *Increasing the size of the solute leads to a significant decrease of* $\mathcal{D}_{\mathrm{im}}$.

Moderately crosslinked solute carriers deviate from this theory. Recently Peppas et al. [67] extended the previous theories to these systems, by describing the normalized solute diffusion coefficient $\mathcal{D}_{\mathrm{im}}/\mathcal{D}_{\mathrm{iw}}$ by the following equation:

$$\frac{\mathcal{D}_{\mathrm{im}}}{\mathcal{D}_{\mathrm{iw}}} = K_1 \; \xi_{\mathrm{p}} \exp \left[-\frac{K_2 r_{\mathrm{d}}^2 \xi_{\mathrm{p}}}{\bar{M}_{\mathrm{n}}^2 (Q_{\mathrm{m}} - 1)}\right] \tag{24}$$

The parameters used here are the same as in eqn. (23) with the exception of the mesh size, ξ_{p}, which describes the average size (as length) of the space between four tetrafunctional crosslinks or four entanglements in the membrane.

In semicrystalline rubbery polymers solute diffusion is significantly slowed down by the crystallites. Diffusion may still be treated by Fickian with effective diffusion coefficient $\mathcal{D}_{\mathrm{im}}'$ defined as

$$\mathcal{D}_{\mathrm{im}}' = \frac{\psi \mathcal{D}_{\mathrm{im}}}{\beta} \tag{25}$$

where $\mathcal{D}'_{\mathrm{im}}$ is the diffusion coefficient in the amorphous rubbery polymer, ψ is the "detour ratio", which accounts for reduction in solute mobility due to the tortuosity of diffusion paths between crystallites, and β is an "immobilization factor" that accounts for physical crosslinking due to the crystallites [68].

In recent contributions in this Journal, Pusch and Walch [69, 70] and Lonsdale [71] offered an overview of recent work on membrane structure and its correlation with permeability and performance, especially for macroporous membranes. Here we examined some recent molecular theories which have applicability to microporous and non-porous membranes and are based on macromolecular physical, rather than macroscopic analysis.

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Notation

c	Total concentration
c_i	Concentration of component i
Đ_{ij}	Multicomponent diffusion coefficient
D_i^{T}	Thermal diffusion coefficient of component i
$\mathcal{D}_{\mathrm{eff}}$	Effective diffusion coefficient
$\mathcal{D}_{ij}$	Effective multicomponent diffusion coefficient
$\mathcal{D}_{\mathrm{im}}$	Nernst–Planck (pseudobinary) diffusion coefficient
$\mathcal{D}_{\mathrm{iw}}$	Diffusion coefficient of solute through solvent
d_i	Generalized driving force ($cRT\,\underset{\sim}{d_i}$) of component i
$\tilde{F}$	Faraday constant
$\underset{\sim}{g}$	Gravity force
$J_i, J_{\mathrm{s}}, J_{\mathrm{w}}$	Flux (flow) of component i
J_{D}	Exchange (volume) flow
J_{v}	Total volume flow
$\underset{\sim}{j_i}$	Flux of component i

K_p	Partition coefficient
K_r	Pore restriction coefficient
L_{ij}	Phenomenological (Onsager) coefficients
L_D	Solute permeability coefficient
L_p	Hydraulic permeability coefficient
L_{pD}, L_{DP}	Permselectivity permeability coefficient
$\overline{M}_c$	Number average molecular weight between crosslinks
$\overline{M}_c^*$	Threshold value of $\overline{M}_c$
M_i	Molecular weight of component i
$\overline{M}_n$	Number average molecular weight of polymer
$\underset{\sim}{N}_i$	Molar flux with respect to a stationary coordinate system
ΔP	Hydraulic pressure difference
P	Pressure
Q_m	Equilibrium volume degree of swelling of membrane
R	Gas constant
r_p	Radius of membrane pore
r_s	Radius of solute
T	temperature
$\overline{V}_i$	Specific volume of component i
$\underset{\sim}{v}_i$	Velocity of component i
$\underset{\sim}{v}_k$	Velocity of component k (solvent or membrane)
$\underset{\sim}{v}_s$	Velocity of solute
$\underset{\sim}{v}_w$	Velocity of solvent
X_i	Generalized (conjugate) forces
x_i	Mole fraction of component i

Greek letters

β	Immobilization factor for diffusion in semicrystalline polymers
ϵ	Porosity of membrane
λ	Ratio of solute to pore radii
μ_i	Chemical potential of component i
ν_i	Ionic charge of component i
ξ_p	Mesh size of chains
$\Delta\pi$	Osmotic pressure difference
ρ	Density of solution
σ	Staverman reflection coefficient of membrane
σ'	Entropy generation
τ	Tortuosity of membrane
υ_2	Polymer volume fraction of membrane
ϕ	Electrostatic potential
ψ	Detour ratio for diffusion in semicrystalline polymers
ω	Solute permeability at zero volume flow
ω_i	Mass fraction of component i

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