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Solute diffusion in swollen membranes
VI. A model for diffusion in heterogeneous media

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Summary

A new model is derived to calculate the solute diffusion coefficient through heterogeneous membranes consisting of a crosslinked, swollen phase and an impermeable, crystalline phase. The solute diffusion coefficient is shown to depend on various structural characteristics of the amorphous permeable phase and on the volume fraction of the impermeable phase.

Introduction

The transport of solute through heterogeneous membranes consisting of two phases is affected by the relative volume fraction of each phase in the system. Of particular interest in separation science is the situation of solute transport through a two-phase system, where one phase is totally impermeable to the solute. Such is the case with solute transport in semicrystalline membranes where the crystallites constitute an impermeable phase, randomly distributed throughout a crosslinked, permeable phase (1). In this case and under ideal conditions (lack of crystallite orientation), the solute diffusivity, permeability and partition coefficients are independent of position in the membrane and constant within each phase.

In this contribution we develop a new model that can be used to calculate the solute diffusion coefficient from knowledge of structural characteristics of the two phases.

Development of Theoretical Model

Solute transport in semicrystalline network membranes occurs only through amorphous regions consisting of amorphous, crosslinked polymer chains and swelling agent. As shown in Figure 1, this type of structure may be approximated by a set of cylindrical, amorphous regions of radii, r, and orientation, ψ, which is specified by the directional and rotational angles, θ and ϕ, respectively. The region surrounding these amorphous structures is an impermeable crystalline phase.

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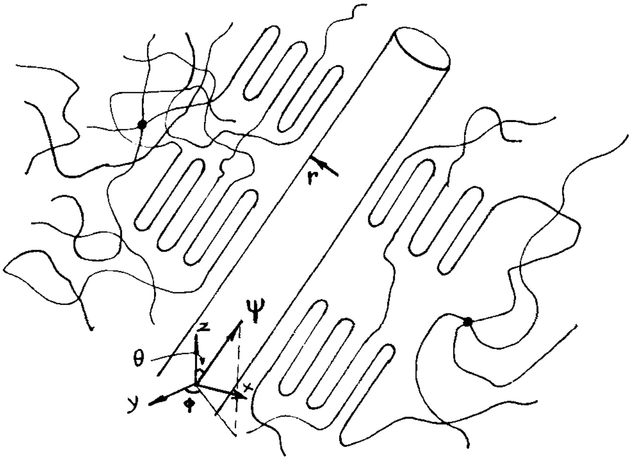

Figure 1. Schematic representation of an equilibrium swollen semicrystalline polymer membrane showing the amorphous "pores" and the crystalline structure creating the walls of the hypothetical cylindrical "pores."

The mass flux of solute i through a given amorphous region is $J_{i,l}(r,l)\ \boldsymbol{\delta}_l(\psi)$. The unit mass flux, $J_{i,l}$, depends only on the radius, r, and the length coordinate of the straight pore segment, l, of any given permeable phase, and the unit vector, $\boldsymbol{\delta}_l$, is a function of the orientation only. If the volume fraction of the amorphous regions per unit radius of amorphous region and orientation ψ is defined as $n(r,\psi)$, then the total average mass flux of solute i over the entire network can be written as

$$\mathbf{J}_i = \int_r \int_\psi \boldsymbol{\delta}_l(\psi)\ J_{i,l}(r,l)\ n(r,\psi)\ dr\ d\psi \tag{1}$$

The unit flux of solute in a given cylinder, $J_{i,l}(r,l)$ can be written as

$$J_{i,l}(r,l) = -\frac{1}{f_l(r)} \cdot \frac{dC_i}{dl} \tag{2}$$

Using equation (1) and (2), the total flux **J** in the form of a vector matrix may be written as follows.

$$[\mathbf{J}] = -\int_r \int_\psi [f(r)]^{-1} \boldsymbol{\delta}_l(\psi)\ (\boldsymbol{\delta}_l(\psi) \cdot \nabla[C])\ n(r,\psi)\ dr\ d\psi \tag{3}$$

where **J** is the vector matrix. The mass flux is also expressed as

$$[J] = - \int_{r=0}^{\infty} [f(r)]^{-1} \kappa(r) \cdot \nabla[C]\, d\upsilon_a'(r) \tag{4}$$

where κ (r) is a second order tensor. This parameter is proportional to the ease by which a molecule travels in the various amorphous regions, and $\upsilon_a'(r)$ is the volume fraction of all the amorphous regions with radii smaller than or equal to r. Here, κ (r) and $\upsilon_a'(r)$ are expressed in functional form as

$$\kappa(r) = \frac{\int_{\psi} \delta_1(\psi)\delta_1(\psi)n(r,\psi)\, d\psi}{\int_{\psi} n(r,\psi)\, d\psi} \tag{5}$$

and

$$\upsilon_a'(r) = \int_{r=0}^{r} \int_{\psi} n(r,\psi)\, d\psi\, dr \tag{6}$$

$$\upsilon_a' = \upsilon_a + \upsilon_s = 1 - \upsilon_c \tag{7}$$

The necessary volume fractions are the equilibrium swelling agent volume fraction, υ_s, the equilibrium amorphous polymer volume fraction, υ_a, and the equilibrium crystalline polymer volume fraction in the swollen state, υ_c.

Equation (4) with the definitions of equation (5) and (6) is the final form of the new model.

Discussion

The final equation of the model (equation (4)) indicates that the solute flux through the heterogeneous system is a function of the volume fraction of the amorphous polymer (i.e. the permeable phase) and the tortuosity of the amorphous diffusional path.

A simplified form can be obtained for the case of uniform amorphous regions. Then, the solute flux may be expressed as

$$J_1 = - \frac{(\upsilon_a + \upsilon_s)\kappa}{f(r_1)} \frac{dC_i}{dx} \tag{8}$$

A solute diffusion coefficient through the semicrystalline polymer, D_c, may be defined according to equation (9)

$$D_c = \frac{(\upsilon_a + \upsilon_s)D_a}{\tau} = \frac{(1-\upsilon_c)D_a}{\tau} \tag{9}$$

In this equation, the scalar quantity τ denotes the tortuosity of the diffusional path in the amorphous regions (2) and replaces its reciprocal value of κ. In addition, the topological factor $f(r_1)$ has been replaced by the solute diffusion coefficient in the amorphous phase, D_a.

The diffusion coefficient D_a refers to the swollen, amorphous, crosslinked portion of the system; it is determined by use of other physical models for diffusion in purely amorphous membranes (3,4). The value of τ is approximately equal to 3.0 for the systems analyzed here (2), and the equilibrium volume fractions, υ_a, υ_s and υ_c, are measured experimentally or predetermined. For example, for diffusion of solutes through a semicrystalline membrane where the *amorphous regions* are *highly swollen,* use of the Peppas-Reinhart model (3) in conjunction with equation (9) leads to the following equation for the calculation of D_c.

$$D_c = \frac{(1-\upsilon_c)D_w}{\tau} f[\frac{\overline{M}_c - \overline{M}_c^*}{\overline{M}_n - \overline{M}_c^*}] \exp [\frac{-\pi r_s^2 l_s \upsilon_a}{V_w \upsilon_s}] \tag{10}$$

Similarly, for solute diffusion in a semicrystalline membrane with *moderately or poorly swollen amorphous regions,* use of the Peppas-Moynihan model (4) gives

$$D_c = \frac{(1-\upsilon_c)D_w}{\tau} f(\upsilon_a^{-3/4}) \exp[k_3(\overline{M}_c - \overline{M}_n) - \pi r^2 l_s \Phi(V)] \tag{11}$$

In both equations, D_w is the solute diffusion coefficient in pure water, r_s is the molecular radius of the solute, l_s is its characteristic size, V_w is the water free volume, $\overline{M}_c$ is the number average molecular weight between crosslinks in the amorphous phase, $\overline{M}_n$ is the number average molecular weight of the polymer before crosslinking, $\overline{M}_c^*$ is the minimum value of $\overline{M}_c$ below which the solute cannot diffuse, $\Phi(V)$ is a function of the free volume of the membrane, and k_3 is a constant (see also ref. (4)).

It is thus concluded, that contrary to previous belief (1), the model of solute diffusion in a heterogeneous system is rather complex and requires incorporation of the structural characteristics of both phases.

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References

1. A. Peterlin, J. Macromol. Sci.-Phys., B11, 57 (1975).
2. R.S. Harland and N.A. Peppas, Proceed. Symp. Controlled Rel. Bioact. Mater., 13, 153 (1986).
3. N.A. Peppas and C.T. Reinhart, J. Membr. Sci., 15, 275 (1983).
4. N.A. Peppas and H.J. Moynihan, J. Appl. Polym. Sci., 30, 2589 (1985).

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