Concentration-Induced Stress Effects in Diffusion of Vapors through Polymer Membranes

MYUNGSOO KIM and P. NEOGI, *Department of Chemical Engineering, University of Missouri, Rolla, Missouri 65401*

Synopsis

There are two types of anomalous diffusion of vapors in solid polymers which are held to be due to swelling. If the latter is seen as strain, then there must be an accompanying stress which can affect the nature and magnitude of diffusion. The theories of diffusion in polymers are examined in light of the network theory of Larché and Cahn. Their formalism is used to solve permeation and sorption in polymer membranes to illustrate the general features of the elastic effects, particularly the time-dependent nature of the solubility. That "anomalous" effects will be present is without doubt, considering the concurrent nature of the added elastic effects. However, the present calculations fail to unearth any behavior similar to the case II diffusion. An order of magnitude estimate has been provided which shows that the effects of elasticity are usually significant in rubbery or amorphous glassy polymers where the anomalous effects occur.

INTRODUCTION

It has long been known that the diffusion of gases and vapor through a polymer membrane gives rise to swelling effects, sometimes so severely as to cause cracking and crazing. It is also speculated that swelling changes the diffusivities and solubilities, hence giving rise to a two-step sorption isotherms.[1,2] Here the first step is due to diffusion, which gives rise to a quick equilibration, and the second step is due to a drift caused by a changing solubility in a swollen polymer. The model explained quantitatively the sorption isotherms, where the rate terms, i.e., diffusivity and the rate of change of solubility, were determined from independent postulates.

The above constitutes a case of anomalous diffusion. Others were soon identified,[3] the most conspicious case being that where the solute enters the polymer not as a smooth profile, but (nearly) as a sharp shock front; this is the well-known case II diffusion. Here it is postulated that behind the shock front is a swollen gel and dry polymer ahead of it. At the front the dry polymer is converted into swollen gel by the action of osmotic pressure. The mechanism is popularly postulated and is considered almost a certainty, as noted in a review.[4]

Proceeding along these lines, it is noted that the swelling can be viewed as a strain. It is well known that the strain or the rate of strain are connected to the stresses in the system through what are known as the constitutive equations. The stress is identified as the osmotic pressure. However, the formulation is yet incomplete, even though these models ostensibly explain the case II diffusion.[5]

Invocation of stress or forces requires *two* equations to be satisfied: the constitutive equation had a force balance equation as noted by Larché and Cahn.[6]

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The theory of how swelling may affect diffusivities are not confined to polymers; alloys and geological systems are affected as well. It is important to recognize the special nature of matrix in which the solute penetrates: The *notion* that the polymer (or other) molecules are arranged spatially with respect to one another remain intact, even when the penetration of the solute distorts such an arrangement.[7] Such solutions are interstitial solutions, in contrast to the conventional solutions which are substitutional.[8] In contrast to considering the solid matrix as a network,[8-11] one has also the cage or free volume theories of diffusion in polymers now in vogue.[12,13] Bueche[14] suggests that the matrix may be approximated as a relatively well-defined cells, occupied by the molecules. The diffusion takes place by jumps, with an activation energy equal to the energy of evaporation. More realism is infused into the model by incorporating the fluctuation of the free volume (cell volume). This affects diffusion since it is less probable for a diffusing molecule to enter a small cell. This constitutes the extrapolation of an earlier suggestion by Barrer[15] that diffusion takes place through the cooperative motion of the polymer molecules, which is taken here to give rise to a fluctuation in the cell volume distribution. Cohen and Turnbull[16] look into the fluctuations of free and occupied cells as a whole and to trace the drift of occupied cells instead of cell to cell migration over activation energy barriers in the previous model. Larché and Cahn[8] assume the matrix to be a network and "hold" it in place. The changes in free energy due to the changes in the permeant solute content is simply $\rho_0 \mu \, dc$, where ρ_0 is the molar volume and, since in this case the permeant solute concentrations are low, in view of the network model is approximately the monomer concentration. μ and c are the chemical potentials and the mole fractions of the permeant solute in that particular medium. One has in this interstitial solution model

$$du_0 = \sigma{:}d\mathbf{E} + T \, ds_0 + \rho_0 \mu \, dc$$

where u_0 and s_0 are the internal energy and the entropy of the system per unit original volume V_0. The σ and $\mathbf{E}$ represent the stress and strain tensors. Obviously the change in the energy of the polymer is due to the work term $\sigma{:}d\mathbf{E}$ of distortion of the network. [For a fluid $\sigma = p\mathbf{I}$, where $\mathbf{I}$ is the unit tensor. Hence $\sigma{:}d\mathbf{E} = pd \, \mathrm{tr}(\mathbf{E})$, where tr represence trace. Further, as $\mathrm{tr}(\mathbf{E}) = \Delta V/V_0$, $\sigma{:}d\mathbf{E}$ reduces to the familiar $p \, dV/V_0$ term in fluids.] A substitutional solution entertains the possibility that the units of the network can be replaced by the permeant molecules; hence

$$du_0 = \sigma{:}d\mathbf{E} + T \, ds_0 + \rho_0(\mu_1 \, dc_1 + \mu_2 \, dc_2).$$

For the present purposes the interstitial solution is the appropriate model. It is noteworthy that, although the model is a discrete one, all formulations used here are continuum.

Larché and Cahn[6] also point out that on sorption by vapor an equilibrium is reached, which is characterized by an equilibrium *stress* (which is chosen by Thomas and Windle[5] to be the osmotic pressure) and an equilibrium *strain* or swelling. That is, the deformation cannot be without limits as it will turn out to be if the stress is related to the rate of strain through a viscosity relation as done by Thomas and Windle. Instead an elasticity relation applies. The equations to be solved therefore are:

$$\text{conservation} \quad \frac{\partial c}{\partial t} = -\nabla \cdot \mathbf{j} \tag{1}$$

$$\text{constitutive} \quad \mathbf{j} = -\frac{Dc}{RT}\nabla\mu \tag{2}$$

$$\text{force balance} \quad 0 = \nabla \cdot \sigma \tag{3}$$

$$\text{constitutive} \quad \sigma = \mathbf{f}(\mathbf{E}^m), \tag{4}$$

where $\mathbf{E}^m$ is the strain due to mechanically applied forces. The strain due to swelling is given by

$$\mathbf{E}^c = \tfrac{1}{3}\,\text{tr}(\mathbf{E}^c)\mathbf{I} \tag{5a}$$

where $\text{tr}(\mathbf{E}^c) = \Delta V^c/V_0$ and eq. (5a) is conventionally rewritten as

$$\mathbf{E}^c = \eta\Delta c\,\mathbf{I} \tag{5b}$$

where η is the appropriate coefficient of linear expansion which is taken to be small and evaluated at $c = c_0$. The Δc represents $c - c_0$. The two strains $\mathbf{E}^m$ and $\mathbf{E}^c$ are additive,

$$\mathbf{E} = \mathbf{E}^m + \mathbf{E}^c \tag{6}$$

and are related to the displacement $\mathbf{u}$ by

$$\mathbf{E} = \tfrac{1}{2}[\nabla\mathbf{u} + (\nabla\mathbf{u})^T] \tag{7}$$

where the superscript T denotes the transpose. Finally, the compatibility condition on $\mathbf{E}$ is

$$\nabla \times \mathbf{E} \times \nabla = 0 \tag{8}$$

Here, the body forces in eq. (3) have been neglected, and it has been assumed that the elastic modulii are sufficiently large such the stress field equilibrates instantaneously compared to the concentration field.

Larché and Cahn[6] show that if the linear relation

$$\mathbf{S}{:}\sigma = \mathbf{E}^m \tag{9}$$

holds exactly, then the relation

$$\mu(\sigma,c) = \mu(0,c) - \frac{1}{\rho_0}\left[\frac{d\mathbf{E}^c}{dc} : \sigma^{\mathrm{T}} + \left(\frac{d\mathbf{S}}{dc} : \sigma^T\right){:}\sigma^T\right] \tag{10}$$

holds *exactly*. The fourth-order compliance tensor $\mathbf{S}$ in this case can be rewritten in the form of constitutive equation (4), linearized to

$$\sigma = \frac{E}{1+\nu}\left[\mathbf{E}^m + \frac{\nu}{1-2\nu}\,\text{tr}(\mathbf{E}^m)\mathbf{I}\right] \tag{11}$$

Note that eq. (9) is Hooke's law, the more general form for (11), Young's law. Substituting eqs. (6) and (5b) into (11), one has

$$\sigma = \frac{\nu E}{(1+\nu)(1-2\nu)}\,\text{tr}(\mathbf{E})\mathbf{I} + \frac{E}{1+\nu}\mathbf{E} - \frac{E\eta\Delta c}{1-2\nu}\mathbf{I} \tag{12}$$

and the compatibility equation expressed in terms of *stress* becomes

$$(1 + \nu)\nabla^2\sigma + \nabla\nabla \, \text{tr}(\sigma) + E\eta \left(\frac{1 + \nu}{1 - \nu} \nabla^2 c\mathbf{I} + \nabla\nabla c\right) = 0 \qquad (13)$$

On contraction Eq. (13) becomes

$$\nabla^2\left[\text{tr}(\sigma) + \frac{2E\eta}{1 - \nu} \, c\right] = 0 \qquad (14)$$

Larché and Cahn[17] have generalized the previous results for large deformations. Here the small deformation theory will be used since that allows one to linearize the constitutive equation (4); the linearity of eq. (4) is an important assumption made by here. A short compilation of the effective Young's modulus E and Poisson's ratio ν has been given by Haward,[18] which are the two parameters obtained on linearization.

If the effect of concentration on the compliance tensor is neglected, then eq. (10) becomes

$$\mu(\sigma,c) = \mu(0,c) - (\eta/\rho_0) \, \text{tr}(\sigma) \qquad (15)$$

Thus eqs. (1)–(3), (13), and (15) are the final equations supplied by them.[6] The boundary value problems to be solved here are those of sorption and permeation vapors in polymeric membranes. The particular point under consideration is to see as to what kind of anomalous diffusion is predicted. If the prediction compares well with the known data, then the anomaly-through-swelling theory discussed earlier is correct. If not, then an essentially irreversible phenomenon gives rise to the anomaly.[19–21]

FORMULATION OF THE BOUNDARY VALUE

The problem consists of solving eq. (3). The solution must also satisfy the compatibility equation (13). As the mole fraction c is not known beforehand, it becomes a very difficult problem. A general solution for an infinite flat plate with no forces acting on the boundaries has been given by Goodier.[22] The solution provides σ in terms of the unknown mole fraction c, and clearly shows that $\text{tr}(\sigma)$, which appears to be a part of the chemical potential in eq. (15), makes the latter dependent on the gross geometry and the boundary conditions. Larché and Cahn[6] point out that then the constitutive equation for the flux, eq. (2), is not a local law anymore.

Traction free membranes cannot be found. One may, however, assume that such tractions, say the vapor pressure p on the two sides of the membrane in the sorption case, are sufficiently small compared to the swelling stresses generated. It also makes it necessary to define a reference mole fraction c_0, where the swelling stresses in a traction free membrane vanishes. The solution to eqs. (3), (13), and (14) is given as

$$\sigma_{xx} = \sigma_{yy} = \frac{\eta E}{1 - \nu} \left(-\Delta c + \frac{1}{L} \int_{-L/2}^{L/2} \Delta c \, dz + \frac{12}{L^3} z \int_{-L/2}^{L/2} z \Delta c \, dz\right) \qquad (16)$$

and $\sigma_{zz} = 0$, where the coordinate system has been explained in Figure 1. One observes that the stresses generated are indeed of an osmotic pressure type, al-
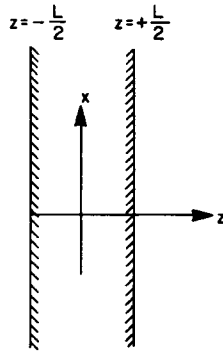
Fig. 1. Geometry of the membrane showing the coordinate system used.

though not completely so. The Δc represents $c - c_0$ and is a function of z alone. Equation (16) yields

$$\text{tr}(\sigma) = \frac{2\eta E}{1 - \nu}\left(-\Delta c + \frac{1}{L}\int_{-L/2}^{L/2}\Delta c\, dz + \frac{12z}{L^3}\int_{-L/2}^{L/2}z\Delta c\, dz\right) \qquad (17)$$

Because of the symmetry both eqs. (13) and (14) reduce to

$$\frac{d^2}{dz^2}\left[\text{tr}(\sigma) + \frac{2E\eta}{1 - \nu}\Delta c\right] = 0 \qquad (18)$$

The solution is

$$\text{tr}(\sigma) = A(t) + B(t)z - 2E\eta\Delta c/(1 - \nu) \qquad (19)$$

which agrees with eq. (17).

Combining eqs. (2), (15), and (17), one has

$$j_z = -D\left[1 + \frac{\partial \ln \gamma}{\partial \ln c} + \frac{2\eta^2 Ec}{RT\rho_0(1 - \nu)}\right]\frac{\partial c}{\partial z} + \frac{24\eta^2 EcD}{\rho_0 L^3 RT(1 - \nu)}\int_{-L/2}^{L/2}z\Delta c\, dz \qquad (20)$$

Here it has been assumed that

$$\mu(0,c) = \mu^0 + RT \ln \gamma c \qquad (21)$$

where μ^0 is a reference potential and γ is the activity coefficient. It entails measuring properties at zero pressure, which cannot be done, or measuring then at the working pressure p and ignoring the difference as small. Thus the role of sorption pressure or the permeation pressures on the stress effect are neglected in solving both the elasticity problem and in the thermodynamic calculations.

When the membrane faces are exposed to the reservoirs where the chemical potential remains constant, one has

$$\mu_R - \mu^0 = RT \ln \gamma\, c + \frac{2\eta^2 E}{\rho_0(1 - \nu)}\left[\Delta c - \frac{1}{L}\int_{-L/2}^{L/2}\Delta c\, dz - \frac{12z}{L^3}\int_{-L/2}^{L/2}z\Delta c\, dz\right] \qquad (22)$$

where μ_R is the reservoir potential. Thus as c changes with time, the concen-

tration at the interface changes with time. If c_∞ is the equilibrium mole fraction, then eq. (22) becomes

$$\mu_R - \mu^0 = RT \ln \gamma \, c_\infty \qquad (23)$$

on assuming that c and c_∞ are not too far apart such that the same value of γ can be used. Substituting into eq. (22) and simplifying for small differences, the solubility is given by

$$\Delta c = \Delta c_\infty - \frac{2\eta^2 E c_0}{\rho_0 RT(1-\nu)} \left[\Delta c - \frac{1}{L} \int_{-L/2}^{L/2} \Delta c \, dz - \frac{12z}{L^3} \int_{-L/2}^{L/2} z \Delta c \, dz \right] \qquad (24)$$

It becomes very intriguing at this point to find out if there exists a relation among c_∞, c_0 and the elastic coefficients. One would have assumed that eq. (22) would yield such results, but it does not, i.e., at equilibrium it yields eq. (23) which does not relate c_∞ to c_0. As explained by Larché and Cahn,[6] the form of eq.(22) varies with the geometry of the sample, i.e., different systems like a semiinfinite system, flat plates, etc., will have different expressions. The key equation is eq. (15), which unifies different geometries. The reason why specific forms under different geometries vary is that the force balances are met differently, i.e., σ varies. For a semiinfinite system, Goodier's method[22] yields $\mathrm{tr}(\sigma) = -[2E\eta/(1 - \nu)]\Delta c$. The solution is also valid for a doubly infinite system and yields, instead of eq. (22),

$$\mu(\sigma, c_\infty) = \mu(0, c_\infty) + \frac{2E\eta^2}{\rho_0(1-\nu)} \Delta c_\infty = \mu_R$$

at equilibrium. This equation can be rewritten as

$$\mu_R = \mu^0 + RT \ln \gamma \, c_\infty + \frac{2E\eta^2}{\rho_0(1-\nu)} \Delta c_\infty$$

and, consequently,

$$\ln \gamma \, c_\infty + N_{El}(c_\infty - c_0) - \frac{(\mu_R - \mu^0)}{RT} = 0, \quad \text{where } N_{El} = \frac{2\eta^2 E}{RT\rho_0(1-\nu)}$$

Thus for small values of N_{El}, c_∞ is dependent both on N_{El} and c_0. However, for large values of N_{El}, $c_\infty \simeq c_0$.

Flory,[9-11] using the theory of rubber elasticity, gives a more complete relation among the various quantities. It is seen there that the elastic strain energies vanish when the volume fraction of the polymer is about 0.67. That is, c_0 is independent of c_∞ and N_{El}.

The shortcoming of Flory's formalism for the present purpose becomes apparent from the fact that it is valid only for an infinite system and an equation such as eq. (22) cannot be derived. It is this equation which one requires to solve as the appropriate problem for the membrane. Thus, although Flory's theory is appropriate for polymers, it is inappropriate when it is used for membranes.[23]

For the small concentrations of the penetrant molecules the activity coefficient γ can be approximated as γ_∞, that at infinite dilution. As a consequence $\partial \ln \gamma / \partial \ln c \simeq \partial \ln \gamma_\infty / \partial \ln c = 0$. Equations (20) and (24) become

$$j_z = -D \left[1 + \frac{2\eta^2 E c}{RT\rho_0(1-\nu)} \right] \frac{\partial c}{\partial z} + \frac{24\eta^2 E c D}{\rho_0 L^3 RT(1-\nu)} \int_{-L/2}^{L/2} z \Delta c \, dz \qquad (25)$$

and

$$\Delta c = \Delta c_\infty - \frac{2\eta^2 E c_0}{\rho_0 RT(1-\nu)} \left(\Delta c - \frac{1}{L} \int_{-L/2}^{L/2} \Delta c \, dz - \frac{12z}{L^3} \int_{-L/2}^{L/2} z \Delta c \, dz \right)$$

(26)

The assumption would imply that the terms quadratic in c are neglected. However, that cannot be done since these are all multiplied by the Young's modulus E, which is a large quantity. [In fact, it has been assumed to be sufficiently large such that the stresses are always balanced: the reason behind the fact that the unsteady state terms are neglected in eq. (3).] Thus with eqs. (25) and (26) the boundary value problems are ready to be posed.

STEADY STATE PERMEABILITY

In this problem the flux j_z is a constant. The nonlinear, implicit equation (25) is still difficult to solve. Nondimensionalizing, one has $p = j_z/(D/L)$, $\zeta = z/(L/2)$, an elasticity number $N_{El} = 2\eta^2 E/RT\rho_0(1-\nu)$, and, eliminating c_0,

$$-p = 2(1 + N_{El}c)\frac{dc}{d\zeta} - 3N_{El}c\lambda$$

(27)

where

$$\lambda = \int_{-1}^{1} \zeta c \, d\zeta$$

(28)

The boundary conditions

$$c\big|_{\zeta=-1} = c_1$$

(29)

and

$$c\big|_{\zeta=+1} = c_2$$

(30)

apply. Integrating (27), one has

$$\frac{1}{3\lambda}\left[\frac{3\lambda + p}{3\lambda N_{El}} \ln \frac{(p - 3\lambda N_{El}c)}{(p - 3\lambda N_{El}c_1)} + c - c_1 \right] = \frac{1}{2}(1 + \zeta)$$

(31)

and

$$\frac{1}{3\lambda}\left[\frac{3\lambda + p}{3\lambda N_{El}} \ln \frac{(p - 3\lambda N_{El}c_2)}{(p - 3\lambda N_{El}c_1)} + c_2 - c_1 \right] = 1$$

(32)

Equations (28), (31), and (32) are sufficient to obtain the permeabilities. One has explicit solutions

$$c = c_1 - \frac{1}{2}(c_1 - c_2)(1 + \zeta)$$

(33)

and

$$p/(c_1 - c_2) = 1$$

(34)

In dimensional form the left-hand side in eq. (34) is $j_z L/D(c_1 - c_2)$, and hence eq. (34) represents classical permeation. From eqs. (17) and (33), one has $\text{tr}(\sigma) = 0$; since $\sigma_{zz} = 0$ and $\sigma_{xx} = \sigma_{yy}$, $\sigma_{xx} = \sigma_{yy} = \sigma_{zz} = 0$. Substituting $\text{tr}(\sigma) = 0$ in Eq. (15) shows that the solubility is classical, i.e., $c_1 = c_{1,\infty}$ and $c_2 = c_{2,\infty}$. Thus, one finds that the steady state permeation is classical. Numerical methods were

used to determine if other solutions were possible; however, they all converged to eqs. (33)–(34).

SORPTION WITH A SOLUBILITY DRIFT

As mentioned earlier, according to some investigators, an anomalous effect is observed in the sorption experiments. The diffusion there is classical, but the solubility changes with time.[1,2] The unsteady state equation for sorption is obtained on combining eqs. (1) and (25),

$$\frac{\partial c}{\partial t} = D\frac{\partial}{\partial z}\left\{\left[1 + \frac{2\eta^2 Ec}{RT\rho_0(1 - \nu)}\right]\frac{\partial c}{\partial z}\right\} \tag{35}$$

and the solubility is on eliminating c_0

$$c = c_\infty - \frac{2\eta^2 Ec_0}{\rho_0 RT(1 - \nu)}\left[c - \frac{1}{L}\int_{-L/2}^{L/2} c\,dz\right] \tag{36}$$

where from symmetry condition

$$\int_{-L/2}^{L/2} z\,\Delta c\,dz = 0 \tag{37}$$

Nondimensionalizing eqs. (35) and (36), with $\tau = 4Dt/L^2$, $\zeta = z/(L/2)$, and $N_{El} = 2\eta^2 E/RT\rho_0(1 - \nu)$, one has

$$\frac{\partial c}{\partial \tau} = \frac{\partial}{\partial \zeta}\left[(1 + N_{Elc)}\frac{\partial c}{\partial \zeta}\right] \tag{38}$$

subject to

$$c\big|_{\zeta=\pm 1} = c_\infty - N_{El}c_0\left(c\big|_{\zeta=\pm 1} - \frac{1}{2}\int_{-1}^{1} c\,d\zeta\right) \tag{39}$$

$$\frac{\partial c}{\partial \zeta}\bigg|_{\zeta=0} = 0 \tag{40}$$

and

$$c\big|_{\tau=0} = c_i \tag{41}$$

One important feature that can be determined from eq. (38) is if it can predict a profile which is discontinuous or near-discontinuous, as appropriate for the case II diffusion. Second-order partial differential equations can be written as

$$au_{\xi\xi} + 2bu_{\xi\tau} + cu_{\tau\tau} + du_\xi + eu_\tau + fu = g$$

where the subscripts indicate partial differentials and u is a function of τ and ξ. Equation (38) can be written as

$$(1 + N_{El}u)u_{\xi\xi} + (N_{El}u_\xi)u_\xi - u_\tau = 0,$$

and on comparison yields $b^2 - ac = 0$, irrespective of whether N_{El} is large or small, or u positive or negative. The conclusion is that eq. (38) remains a parabolic equation under all conditions, and, since only the solution to a hyperbolic equation can show discontinuity,[24] case II will not be predicted here.

The case of small values of N_{El} is dealt with in the Appendix. The behavior

is near-Fickian but with a changing solubility with time. The result in dimensional form for the solubility is

$$\frac{c - c(0)}{c_\infty - c(0)} \sim 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{e^{-(2n+1)^2\pi^2\tau/4}}{(2n+1)^2} \tag{42}$$

where $c(0)$ is the solubility at $\tau = 0$.

The case for large N_{El} is treated in the Appendix. It provides somewhat strange results: To the first approximation, the concentration is same everywhere but changes with time. This is also its time-dependent solubility, given by

$$\frac{c - c(0)}{c_\infty - c(0)} = \frac{1 - e^{-3\tau}}{1 + (c_\infty/c_i - 1)e^{-3\tau}} \tag{43}$$

and $c = c_\infty$ if c_i is zero as explained in the Appendix. At $\tau = 0, c$ is c_i. As mentioned previously $c_\infty \approx c_0$ at large values of N_{El}.

Considering the parabolic nature of eq. (38), one may define an average value for the effective diffusivity $D[1 + N_{El}c]$ as $D[1 + N_{El}\langle c \rangle]$, as discussed elsewhere.[25] Equation (38) becomes

$$\frac{\partial c}{\partial \tau} = \frac{\partial}{\partial \zeta}\left[(1 + N_{El}\langle c \rangle) \frac{\partial c}{\partial \zeta}\right] \tag{44}$$

subject to eqs. (40)–(41) and an unknown solubility $c|_{\zeta=\pm 1} = \phi(\tau)$. The solution with Laplace transforms is well known[25]; one obtains

$$\bar{c} = \left(\bar{\phi} - \frac{c_i}{p}\right) \frac{\cosh(\alpha\zeta)}{\cosh(\alpha)} + \frac{c_i}{p} \tag{45}$$

where $\alpha = [p/(1 + N_{El}\langle c \rangle)]^{1/2}$, p is the variable of transformation, and the overbars indicate transformed quantities. Taking the Laplace transform of eq. (39) and substituting eq. (45), one has

$$\bar{\phi} = \frac{u_\infty}{N_{El}c_0} - u_i\left(\frac{\tanh \alpha}{\alpha} - 1\right)\bigg/ p\left(\frac{1}{N_{El}c_0} + 1 - \frac{\tanh \alpha}{\alpha}\right) \tag{46}$$

Inverting eq. (46) with Heaviside formula, one has

$$\phi = c_\infty - \sum_{n=1}^{\infty} \frac{2(c_\infty - c_i)}{1 - (1/N_{El}c_0)(N_{El}c_0 + 1)^2\xi_n^2} \exp[-(1 + N_{El}\langle c \rangle) \cdot \xi_n^2\tau] \tag{47}$$

where the ξ_n are the infinite roots of

$$\frac{\tan \xi_n}{\xi_n} = 1 + \frac{1}{N_{El}c_0} \tag{48}$$

The solution is valid for all values of N_{El}.

RESULTS AND DISCUSSION

Before commenting on the results obtained here, it is important to assess the role of elasticity in diffusion in general. In the problem posed here its magnitude is governed by the dimensionless quantity $2\eta^2 E/\rho_0 RT(1 - \nu)$. For polymer density ~ 1 g/cm^3 and the molecular weight of the repeat units ~ 20, $\rho_0 \sim 0.05$ mol/cm^3. $E \sim 10^{11}$ dyn/cm^2, $\nu \sim 0.3$, and $\eta \sim 0.1$ for glassy polymers,[15,5] and,

at $300°K$, $2\eta^2 E/\rho_0 RT(1 - \nu) \sim 2$, a significant quantity. For rubbery polymers η could be higher, say ~ 1.0, but E is lower $\sim 10^8$ dyn/cm^2 and the figure is ~ 0.2.

The distinctive features of the elastic effects are listed below:

(a) The nature and the strength of the effects vary from one geometric configuration to another.[6] The aspects of thin membrane have been discussed here.

(b) The effects also vary if the concentration profile is symmetric or asymmetric, e.g., there is a symmetry in the sorption case. Further, the stresses vanish at equilibrium and at steady state, irrespective of the above consideration. The stresses exist only under unsteady state conditions.

(c) Anomalous effects observed in sorption is that of time-dependent solubility, the effective diffusion is Fickian. The results appear to explain some of the known experimental data.[1,2] It is noteworthy that only an effective diffusivity can be obtained from sorption studies but exact values can be obtained from the permeation experiments.

(d) Case II cannot be explained with the swelling effects as formulated here.

One of the questions raised here has not been answered fully, viz., the nature of the relation among c_0, c_∞, and N_{El} in membranes. The relationship can be found for an infinite or a semiinfinite system; however, whether they apply to membranes is not known. It is noteworthy that such a relation is needed only under unsteady state conditions; at steady state or at equilibrium, c_∞ is unaffected by c_0 or N_{El}.

CONCLUSIONS

Larché and Cahn[6] have shown that the coupling between a concentration field and a stress field is strongly governed by the nature of the boundaries. Specific solutions have been obtained here for a membrane under conditions of steady diffusion. Anomalous effects are found mainly in the form of time-dependent solubility. It is also found that not only is the nature of diffusion in a membrane different from an infinite or semiinfinite system, it also differs if the concentration profile is symmetric (as in sorption) from that when it is asymmetric (as in permeation). For polymers, it is seen that the elastic effects can modify the results, sometimes by an order of magnitude.

APPENDIX

For small values of N_{El} one assumes a solution of the form

$$c \sim c^{(0)} + N_{El}c^{(1)} + O(N_{El}^2) \tag{49}$$

Substituting eq. (49) into eqs. (38)–(41), one has

$$\frac{\partial c^{(0)}}{\partial \tau} = \frac{\partial^2 c^{(0)}}{\partial \zeta^2} \tag{50}$$

$$c^{(0)}|_{\zeta = \pm 1} = c_\infty \tag{51}$$

$$\frac{\partial c^{(0)}}{\partial \zeta}\bigg|_{\zeta=0} = 0 \tag{52}$$

$$c^{(0)}\big|_{\tau=0} = c_i \tag{53}$$

as $N_{El} \to 0$. The solution is known as[26]

$$c^{(0)} = c_\infty - \frac{4(c_\infty - c_i)}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} e^{-(2n+1)^2 \pi^2 \tau/4} \times \cos \frac{(2n+1)\pi\zeta}{2} \tag{54}$$

One may now proceed to obtain $c^{(1)}$, which shall not be done here, for $c^{(1)}$ is in main part a correction to $c^{(0)}$ for the concentration dependence of the effective diffusion coefficient $D[1 + N_{El}c]$, as seen in eq. (35). Such effects from concentration dependence of the diffusivity holds little secrets or significant departures from the Fickian behavior.[25] In fact, one may substitute an effective diffusivity D_a in an appropriate way.[25] The novelty here is the boundary condition (36) or (39). Substituting eqs. (49) and (51) into eq. (39), dividing with N_{el} and taking the limit $N_{El} \to 0$, one has

$$c^{(1)}\big|_{\zeta=\pm 1} = -c_0\left[c^{(0)}\big|_{\zeta=\pm 1} - \frac{1}{2}\int_{-1}^{1} c^{(0)}\,d\zeta\right] \tag{55}$$

Substituting eq. (54) into eq. (55), one has

$$c^{(1)}\big|_{\zeta=\pm 1} = -\frac{8c_0(c_\infty - c_i)}{\pi^2} \sum_{n=0}^{\infty} \frac{e^{-(2n+1)^2\pi^2/4}}{(2n+1)^2} \tag{56}$$

A quantity of particular interest here is

$$\frac{c\big|_{\zeta=\pm 1} - c_i}{c_\infty - c_i} \sim 1 + \frac{N_{El}}{(c_\infty - c_i)} c^{(1)}\big|_{\zeta=\pm 1} \tag{57}$$

For large values of N_{El}, one chooses a series

$$c \sim c^{(0)} + N_{El}^{-1} c^{(1)} + O(N_{El}^{-2}) \tag{58}$$

Substituting eq. (58) into eqs. (38)–(41), one has

$$0 = \frac{\partial}{\partial \zeta}\left(c^{(0)} \frac{\partial c^{(0)}}{\partial \zeta}\right) \tag{59}$$

$$c^{(0)}\big|_{\zeta=\pm 1} = \frac{1}{2}\int_{-1}^{1} c^{(0)}\,d\zeta \tag{60}$$

$$\frac{\partial c^{(0)}}{\partial \zeta}\bigg|_{\zeta=0} = 0 \tag{61}$$

and

$$c^{(0)}\big|_{\tau=0} = c_i \tag{62}$$

on taking the limit $N_{El} \to \infty$.

The solution is

$$c^{(0)} = \alpha_1(\tau) \tag{63}$$

where α_1 is an unknown function of time τ.

Substituting eqs. (58)–(63) in eqs. (38)–(41) and taking the limit $N_{El} \to \infty$ (after dividing with N_{El}^{-1} where appropriate) one has

$$\frac{1}{\alpha_1}\frac{d\alpha_1}{d\tau} = \frac{\partial^2 c^{(1)}}{\partial \zeta^2} \tag{64}$$

$$\alpha_1 = c_\infty - c_0\left[c^{(1)}\big|_{\zeta=\pm 1} - \frac{1}{2}\int_{-1}^{1} c^{(1)}\,d\zeta\right] \tag{65}$$

$$\frac{\partial c^{(1)}}{\partial \zeta}\bigg|_{\zeta=0} = 0 \tag{66}$$

The solution is

$$c^{(1)} = \frac{1}{2\alpha_1}\frac{d\alpha_1}{d\tau}\zeta^2 + \alpha_2(\tau) \tag{67}$$

where α_2 is an unknown function of τ. Substituting into eq. (65) and simplifying, one has

$$\frac{d\alpha_1}{d\tau} - \frac{3c_\infty}{c_0}\alpha_1 = -\frac{3\alpha_1^2}{c_0} \tag{68}$$

which is Bernoulli's equation. The solution subject to Eqs. (62) and (63) is

$$\alpha_1 = \left[\frac{1}{c_\infty} + \left(\frac{1}{c_i} - \frac{1}{c_\infty}\right)e^{-3c_\infty\tau/c_0}\right]^{-1} \tag{69}$$

From the nature of $c^{(0)}$, Eq. (69) represents the solubility to the first approximation. One also has the solubility expressed as

$$\frac{c - c_i}{c_\infty - c_i} = \left\{\left[\frac{1}{c_\infty} + \left(\frac{1}{c_i} - \frac{1}{c_\infty}\right)\exp(-3c_\infty\tau/c_0)\right]^{-1} - c_i\right\}\bigg/ (c_\infty - c_i) \tag{70}$$

Further, if $c_i = 0$, $c = c_\infty$ at all times.

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