Solute Diffusion in Swollen Membranes. IX. Scaling Laws for Solute Diffusion in Gels

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Synopsis

A scaling law was developed for the diffusion coefficient of spheroidal and ellipsoidal solutes in nonporous, equilibrium-swollen hydrogels. The law relates the solute diffusion coefficient to the solute size, the gel mesh size, and the gel equilibrium volume degree of swelling. The law was verified by appropriate data of low and high molecular weight solute diffusion through hydrogels such as swollen networks of poly(vinyl alcohol), poly(2-hydroxyethyl methacrylate), cellulose, and others. An additional scaling law was developed which relates the rate of release of a small or large molecule from an equilibrium swollen hydrogel with time and with morphological characteristics of the polymeric network.

INTRODUCTION

Since deGennes' proposal of relationships between macromolecular statistics and phase transition problems, scaling concepts have been used successfully in polymer science. Scaling concepts distinguish length scales of homogeneous chemical interaction and material. Chemical interactions are defined in terms of pair correlations between monomers. A correlation function is a spatial distribution of monomers about any given monomer. Thus, scaling concepts avoid a great magnification of the medium to be described by neglecting local interactions and confining attention to a more panoramic view. The use of this global perspective leads to development of simple, universal relationships for polymeric media in a given set of conditions.

In a scaling analysis, only the functional dependence of a set of parameters on a given quantity is desired. The resulting scaling law gives the correct relationship between parameters under a given set of conditions for all materials of interest. Only certain constants may be material dependent. This type of problem-solving approach is particularly useful in cases where exact expressions are prohibitively complex to derive or use. It will be shown that scaling concepts can be used to understand the relationships between structure and diffusive transport through polymers.

First, it is useful to consider the diffusion of a tagged molecule in a simple liquid. The molecule moves by a succession of random walks in which the mean free path is much smaller than its diameter.[1] We wish to develop a relationship between the size of this solute and its diffusion coefficient in a dilute solution. In this analysis it is convenient to use a hydrodynamic radius

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Journal of Applied Polymer Science, Vol. 36, 735–747 (1988)
 CCC 0021-8995/88/040735-13$04.00

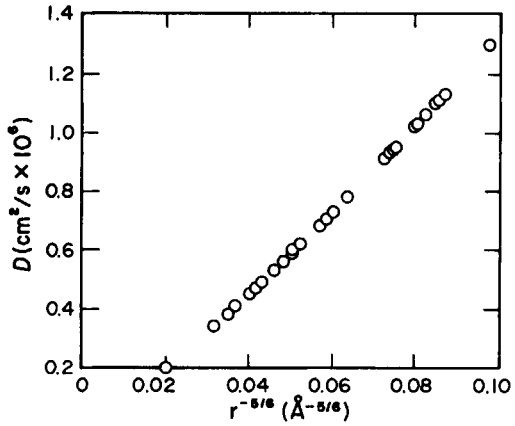

Fig. 1. Overall dependence of the solute diffusion coefficient, $D_{3,12}$ (cm^2/s), on the solute size, r (Å), in deionized water at 20°C.

R_h, defined by a sphere of equivalent volume to that of the molecule, to characterize the molecular size of the solute. For nonspherical molecules which are not smaller than the solvent molecule, the diffusion coefficient D is a function of this radius. The well-known scaling law is

$$D \cong R_h^{\zeta} \tag{1}$$

where ζ is close to $-5/6$. Figures 1 and 2 include data of diffusion coefficients of a wide range of nonspherical solutes in deionized water at 20°C and in an isotonic saline solution at 37°C, respectively,[2-7] vs. their hydrodynamic radius to the $-5/6$ power. These data are for solutes of molecular weight from 60 (urea) to 66,000 (bovine serum albumin). This scaling law is particularly useful as it applies to any solute diffusing through a fluid, without consideration of the diffusional mechanism.

Figure 3 gives a depiction of the physical model considered for solute diffusion through a nonporous gel. This is a three-component system including

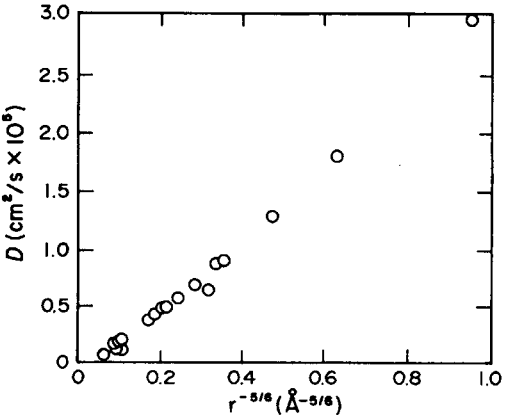

Fig. 2. Overall dependence of the solute diffusion coefficient, $D_{3,12}$ (cm^2/s), on the solute size, r (Å), in isotonic saline at 37°C.

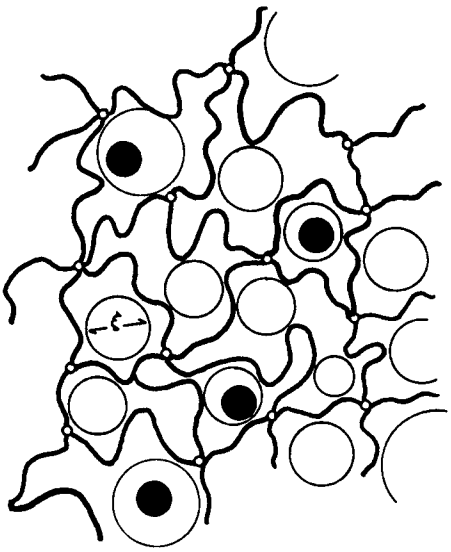

Fig. 3. Crosslinked structure of a polymer gel, showing effective chains of the structure defined by crosslinks. The effective area for diffusion for the solute is characterized by an average mesh size ξ. The smaller solutes, illustrated as dark circles, must pass between the macromolecules.

a polymer network, which is in swelling equilibrium with a solvent, and an inert solute which is small in size with respect to the length of the polymer chains. Many solutes, such as bioactive agents, can be modeled as relatively small spheres, spheroids, or ellipsoids which diffuse through the gel macromolecular network.

A gel has a crosslinked polymer structure where the crosslinks (junctions) define effective chains. We may identify the radius of gyration of a chain between crosslinks, R_s, as a correlation length in the macromolecular network. The hydrodynamic screening caused by the network of polymer requires the solute's path to be tortuous. An average correlation length or mesh size, ξ, measured by neutron scattering[8] or quasielastic light scattering,[9] characterizes the network and the effective space available for solute diffusion. Here

$$\xi = R_s = Q^{1/3}N^{1/2}l \tag{2}$$

where Q is the volume degree of swelling, N is the number of links in the chain, and l is the bond length (for —C—C— bonds).

The "blob" models as proposed by deGennes[10] can be used to quantify the degree of swelling of an effective polymer chain. Inside one blob or "sphere of influence" the chain does not interact with other chains. Here we identify the blob diameter with the mesh size or correlation length. Chains of sufficiently high molecular weight experience excluded-volume-induced swelling, and the mesh size in a semi-dilute solution obeys

$$\xi \cong l(1 - 2\chi)N^{3/5} \tag{3}$$

where $(1 - 2\chi)$ is the excluded volume per monomer and χ is Flory's reduced residual partial-molar free energy of dilution.[11]

In the simple blob model of swollen coils, there is a critical degree of polymerization at which the expression for the mesh size changes from eq. (2) to eq. (3). The polymer gel in swelling equilibrium with a good solvent can be considered as a set of closely packed coils kept together by crosslinks and permanent entanglements. Thus, processes in polymer solutions are very similar to those in swollen gels. The deGennes c^*-theorem postulates that the chains in the semidilute gel automatically maintain an equilibrium concentration c_e proportional to the concentration at which free coils just overlap in free solution, c^*. At this transition concentration, the range of pair correlations is equal to the mean distance between chains. The scaling law is

$$c_e \cong k(z)N_p^{-4/5}(1 - 2\chi)l_p^{9/5} \tag{4}$$

where $k(z)$ is a constant number of order unity depending on the crosslinking functionality z, l_p is the persistence length, and N_p is the number of links in this length. In the limit of infinite chain links, the correlation length then obeys the concentration dependence[8,12-14]

$$\xi \cong \phi^{-3/4} \tag{5}$$

At the transition concentration $\tilde{\phi}$, the excluded volume is screened by the coils whose interactions are very weak and binary interactions dominate. A strict blob model no longer pertains since the coils approach the unperturbed state where eq. (2) applies. This state is called the "theta solvent" state, where the radius of gyration obeys the following concentration dependence[13,15-19] in the limit of infinite chain links:

$$\xi \cong \phi^{-1/2} \tag{6}$$

In general, the correlation length may be written as

$$\xi \cong \phi^m \tag{7}$$

The exponent m indicates the concentration dependence reflecting monomer-pair correlations.[14]

Scaling concepts in diffusion have been previously confined to cooperative and tube diffusion. The cooperative or mutual motions of a collection of chains are osmotic responses to fluctuations in local solvent concentrations. The translational diffusion of a linear polymer trapped in a network is a reptation process.[20]

The description of small solute diffusion in polymer solutions and gels has been traditionally confined to the mass transfer theories of the Stefan–Maxwell equations and the principals of irreversible thermodynamics. These two approaches are based on the application of continuum mechanics which postulates macroscopic material properties which vary continuously with (i) the size of a differential volume of material considered, (ii) the position in the material system, and (iii) time.[21,22] Each of these approaches explains the relation of diffusional flux to the applied driving forces. The Stefan–Maxwell approach uses multicomponent diffusivities for pairs of com-

ponents which are material and system properties of the components. The irreversible thermodynamic approach considers the diffusion coefficient as the linear or phenomenological coefficient for the flux resulting from a concentration gradient force. Peppas and Meadows[22] recently reviewed these theories as applied to mass transport in polymer membranes.

Here we present new scaling laws of the solute diffusion coefficient with polymer structural characteristics which are applicable to gels.

DERIVATION OF A NEW SCALING LAW

It is desirable to relate the dependence of the solute diffusion coefficient through a gel on the structural parameters of the polymer. The diffusion process can be treated by Eyring's rate theory as described earlier since there exist barriers to the translational movement of the solute in the gel. According to the Eyring theory, the diffusion coefficient of a solute, D_3, has the scaling law form of

$$D_3 \cong T\nu e^{-\Delta G^+/kT} \cong T\nu e^{-\Delta H^+/kT} e^{-\Delta S^+/k} \tag{8}$$

where T is the absolute temperature, ΔG^+, ΔH^+, and ΔS^+ are the free energy, enthalpy, and entropy of activation, respectively, and ν is the translational oscillating frequency of the diffusing molecule. This equation may be applied to describe both the solute diffusivities in the gel, $D_{3,12}$, and in the pure solvent, $D_{3,1}$. The activation enthalpy and oscillating frequency depend on the temperature and polymer properties. In ideal systems, the enthalpy of activation is independent of concentration. The solute diffusion coefficient in the gel normalized by the diffusion coefficient in pure solvent, $\hat{D}$, obeys eq. (9), under the assumption that the activation enthalpies and the oscillating frequencies in the two media remain constant, which is reasonable for dilute and chemically inert systems:

$$\hat{D} \equiv \frac{D_{3,12}}{D_{3,1}} \cong \frac{e^{-\Delta S^+_{3,12}/k}}{e^{-\Delta S^+_{3,1}/k}} \tag{9}$$

The activation entropy can be expressed as a probability of activation, P^+, as follows:

$$S^+ \cong k \ln P^+ \tag{10}$$

Upon substituting the respective probabilities from eq. (10) into eq. (9), the normalized diffusion coefficient can be expressed as a ratio of translational probabilities as in

$$\hat{D} = \frac{P^+_{3,12}}{P^+_{3,1}} = \frac{P^-_{3,12} P^{|}_{3,12}}{P^+_{3,1}} \tag{11}$$

The probability $P^+_{3,12}$ contains two important contributions: (i) the probability of finding in the medium an opening or unhampered space equal to or larger than the size of the solute; and (ii) the conformational probability of

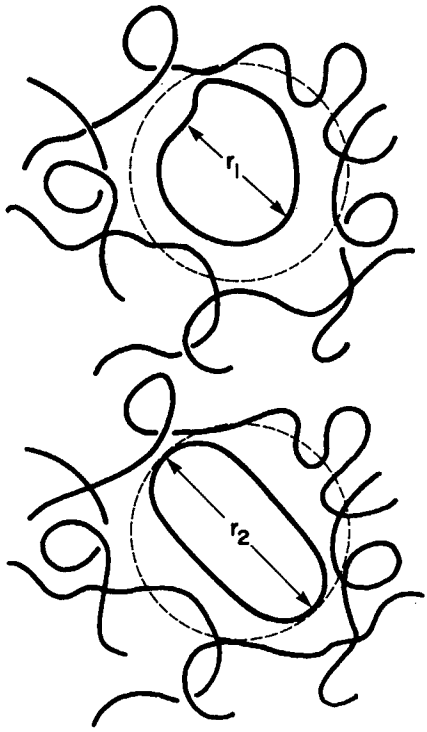

Fig. 4. Sieve mechanism showing that solutes of different shapes but identical cross-sectional areas must pass through the same average mesh opening.

the network forming a volume sufficiently large for the passage of the solute in one jump. Therefore, the translational probability in the gel, $P^{+}_{3,12}$, can be broken into two components: (i) the probability of moving through the free volume, $P^{-}_{3,12}$; and (ii) the probability of moving through the gel mesh, $P^{|}_{3,12}$. Since these actions are simultaneous, the overall probability is simply the product of the aforementioned probabilities.

The novelty of this derivation is the calculation of the probability of a solute of characteristic size r to pass through an opening of size ξ, which describes the sieving mechanism of the diffusion process. There are two ways of describing this probability, either as the ratio of the sizes, $1 - r/\xi$, or as the ratio of the areas, $1 - (r/\xi)^2$. The parameter r characterizes the solute size by means of the radius of a sphere equivalent to the volume of the solute. Figure 4 illustrates this problem by showing two solutes of equal cross-sectional area but different ellipsoidal shapes passing through the same mesh opening. This figure illustrates that solute 1 stands a better probability of passing through the opening than solute 2. It is concluded that the probability is a function of the ratio of the sizes, and it is assumed that there is a linear dependence of the screening probability on the ratio of sizes.

$$P^{|}_{3,12} \cong 1 - r/\xi \tag{12}$$

Thus, the probability for the inert solute passing through a macromolecular screen decreases linearly as the solute approaches the size of the opening.

Free-volume theory can be used to determine the conformal probability of forming a hole sufficiently large for the passage of the solute in the swollen gel. Following the analysis of Yasuda et al.[23] and Peppas and Reinhart,[24] the free-volume theory provides the desired conformal probability. Equations (13) and (14) provide the probabilities of finding the required free-volume in the gel and solution, respectively,

$$P_{3,12}^{-} \cong e^{-\gamma v^*/V_{f,12}} \tag{13}$$

$$P_{3,1}^{+} \cong e^{-\gamma v^*/V_{f,1}} \tag{14}$$

Here γ is a factor ($1/2 \leq \gamma \leq 1$) which corrects for the overlap of free volumes associated with two or more proximal molecules, v^* is the volume displaced by the solute in one diffusional jump, and $V_{f,1}$ is the specific free volume of the ith component. The displaced volume can be expressed as a function of the solute size since it is equal to the cross section, πr^2, times the jump length, λ_d. The ratio of these probabilities is then

$$P_{3,12}^{-}/P_{3,1}^{+} \cong e^{-(\gamma v^*)(1/V_{f,12}-1/V_{f,1})} \tag{15}$$

The free-volume of the membrane can be written in terms of the free volumes of the solvent and the polymer as shown in

$$V_{f,12} = \phi_1 V_{f,1} + \phi_2 V_{f,2} \tag{16}$$

Since the diffusion coefficient of the solute in a dry polymer network is several orders of magnitude smaller than that in a swollen gel, it is reasonable to neglect the polymer contribution to the free volume available for solute diffusion in the gel.[23,24] Then

$$V_{f,12} \simeq \phi_1 V_{f,1} \tag{17}$$

This approximation is quite accurate since $V_{f,2}$ is typically 2.5% at 25°C. Upon combination of eqs. (15) and (17), we obtain

$$P_{3,12}^{-}/P_{3,1}^{+} \cong e^{[-Y/(Q-1)]} \tag{18}$$

where

$$Y \equiv \gamma \pi r^2 \lambda_d / V_{f,1} \simeq 1 \tag{19}$$

and

$$Q = 1/\phi_2 \tag{20}$$

Here Q is the volume degree of swelling for the gel and Y is a structural parameter, near unity, which is proportional to r^2.[24] In effect, Y is a scale factor for the ratio of the volume displacement per diffusional jump to the free-volume contribution per molecule of solvent. The next section discusses evidence for the claim *that a unit value of Y is a useful approximation.*

The final form of the scaling expression for the normalized diffusion coefficient results after combining eqs. (11), (12), and (18):

$$\hat{D} \equiv D_{3,12}/D_{3,1} \cong [1 - r/\xi]e^{[-Y/(Q-1)]} \tag{21}$$

In cases where the mesh size ξ is unknown, it is possible to extend the previous scaling analysis to semidilute, isotropic gels. In the semidilute state, the mesh size obeys the known[20] scaling law:

$$\xi \cong l^3 c_2^{-3/4} \tag{22}$$

For the polymer, assuming a constant molar volume, we may write

$$\phi_2 = 1/Q = c_2\bar{v} \cong c_2 \tag{23}$$

Therefore,

$$\xi \cong Q^{3/4} \tag{24}$$

Combination of eqs. (21) and (24) leads to the equivalent scaling law for the semidilute state:

$$\hat{D} \equiv D_{3,12}/D_{3,1} \cong rQ^{-3/4}e^{[-Y/(Q-1)]} \tag{25}$$

This completes the formal derivation of the new scaling law for solute diffusion in equilibrium swollen gels. It applies for:

i. solutes sufficiently small with respect to the network mesh size to avoid entangling with the polymer chains, i.e., $r < \xi$;
ii. nonporous gels;
iii. chemically inert solutes and gels.

RESULTS AND DISCUSSION

Verification of the scaling law may be done by use of existing diffusion data. In this analysis two parameters of importance are the volume degree of swelling, Q, and the mesh size ξ of membranes and gels. Korsmeyer and Peppas[25] and Peppas and Reinhart[24] presented experimental determinations of both ξ and Q. Since the authors did not use the relationship of eq. (24), Figure 5 is a plot of ξ vs. $Q^{3/4}$ based on their data. The correlation coefficients are 0.996 and 0.9998 for the lines of the data of Korsmeyer and Peppas[25] and Peppas and Reinhart,[24] respectively. These results clearly support the new scaling law.

Equation (21) shows the effect of the structural parameters on the normalized diffusion coefficient under the conditions mentioned previously. Since no account has been made of material interactions, a plot of the right-hand side of eq. (21) vs. the left-hand side yields a straight line. According to the scaling mathematical framework employed, the unspecified slope and intercept depend on the polymer-solvent pair considered.

The data presented in Figures 6 and 7 provide support for the final scaling law.[3,25-29] It is assumed that the material constant Y is unity for all cases. We

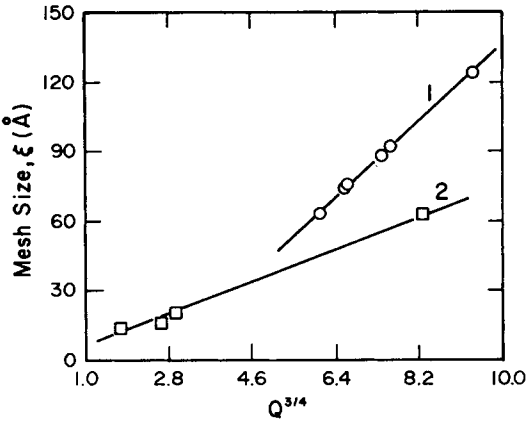

Fig. 5. Mesh sizes vs. equilibrium volume degree swelling Q, plotted as $Q^{3/4}$, in semidilute gels of PHEMA (1) and PVA (2). Correlation coefficients are 0.998 and 0.996, respectively. Data from Refs. 25 and 26.

will reconsider this assumption later. Figure 6 is a plot of the normalized diffusion coefficient versus the right-hand side terms of eq. (21). Each line represents data for solute diffusion coefficients determined experimentally for hydrophilic membranes swollen to equilibrium in water. The membranes vary due to the degree of crosslinking, and, consequently, also due to the mesh size and equilibrium volume degree of swelling. Figure 7 is a similar plot of the left-hand side terms of eq. (25) vs. the right-hand side terms. The data are for different sizes of solutes through two different gels. Good correlation coefficients result from a linear regression analysis in all cases.

Table I summarizes the nonlinear regression analysis on these data. Here a nonlinear regression algorithm was used to determine the rms residuals based

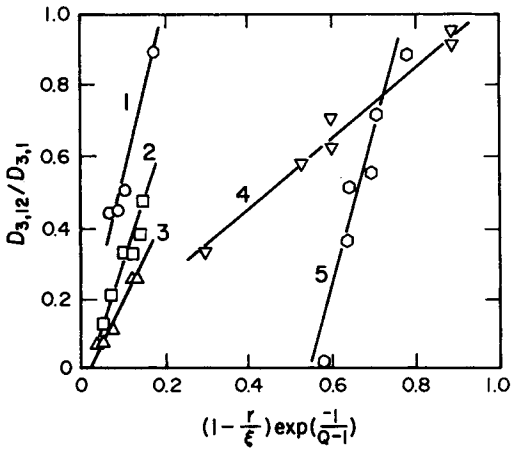

Fig. 6. Dependence of the normalized diffusion coefficient $D_{3,12}/D_{3,1}$ on the term $(1 - r/\xi)\exp[-1(Q - 1)]$. Data presented are for (1) salicylic acid (correlation coefficient $\rho = 0.975$) through PHEMA,[29] (2) progesterone ($\rho = 0.982$) through p(HEMA-co-MEMA) hydrogels with EGMA,[28] (3) progesterone ($\rho = 0.953$) through p(HEMA-co-MEMA) hydrogels with TEGDMA,[28] (4) theophylline ($\rho = 0.991$) through PVA,[25] and (5) bovine serum albumin ($\rho = 0.953$) through PVA.[26]

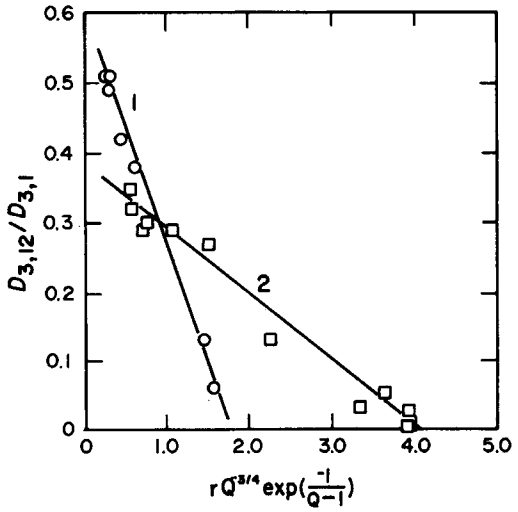

Fig. 7. Dependence of the normalized diffusion coefficient $D_{3,12}/D_{3,1}$ on the term $rQ^{-3/4}$ $\exp[-1/(Q-1)]$. Data presented are for various solutes through (1) heparinized PVA[3] (correlation coefficient $\rho = -0.990$) and (2) Avisco wet gel[3] ($\rho = 0.971$).

on best fitted values of Y and values of unity by contention. Except for the case of bovine serum albumin diffusion,[27] the nonlinear regression results in a best-fitted value for Y close to unity. The smaller value of Y seems physically realistic since albumin is much larger than the other solutes. Here the smaller diffusional jump length for the larger solute could be due to inertial effects. Unfortunately, none of the cited investigations include confidence intervals in their results by experimental replication. For practical considerations, there is little, if any, difference in the root-mean-square of the residuals between the best-fit determination of Y and the case where Y is assumed to be unity. Typically, diffusion coefficients are determinable within 15%; the probable scattering of data cannot justify distinction between the two regression analyses. This small amount of available data lends support to the notion that Y is near unity, and the scaling analysis has good correlative value. It is also apparent that $Y = 1$ is a useful approximation as the model is relatively insensitive to this parameter. It is clear, however, that additional studies including statistical replications would be quite valuable.

TABLE I
Nonlinear Regression Fitting of Model Parameter Y of Eq. (21) and Linear Regression of Literature Data for $Y = 1$

Data group	Best-fit value of Y	RMS residual	RMS residual ($Y = 1$)
Bovine serum albumin	0.13	0.11	0.06
Theophylline	0.69	0.05	0.04
Progesterone	1.05	0.03	0.02
Progesterone	0.55	0.04	0.05
Avisco wet gel	0.80	0.09	0.08
Heparinized PVA	0.75	0.02	0.02

As an example of the utility of eq. (21), the reader should consider the first 60% of Fickian solute release from an equilibrium swollen gel in the shape of a long slab into a perfect sink. The fraction of solute released, M_t/M_∞, obeys[30]

$$Mt/M_\infty = \left[4D_{3,12}t/\pi L^2\right]^{1/2} \tag{26}$$

where L is the slab half-thickness.

To find the structural effects on the rate of solute release, eq. (26) may be differentiated and substituted into eqs. (1) and (21) to obtain

$$\frac{dM_t}{M_\infty\, dt} \cong \frac{D_{3,12}^{1/2}}{L} t^{-1/2} \cong r^{-5/12}\left[1 - \frac{r}{\xi}\right]^{1/2} \exp\left[\frac{-Y}{2(Q-1)}\right] \tag{27}$$

where

$$Y \cong r^2 \tag{28}$$

The structural parameters of the gel strongly affect the solute diffusivity and thus the rate of release. In addition, the solute release rate is a very complicated function of its size.

Both structural parameters ξ and Q of the gel are concentration-dependent by definition, the equilibrium volume degree of swelling is the reciprocal of the equilibrium polymer volume fraction. The concepts summarized by eq. (21) and the unified theory for the mesh size correlation length concentration dependence can be combined. Figure 8 illustrates the theoretical results over the semidilute to concentrated regimes and the effect of increasing the relative solute size. The typical solute size r is arbitrarily taken as 1/10 of the mesh size ξ evaluated[14] at a polymer concentration ϕ^*. This figure shows that an increase in the polymer concentration reduces the solute diffusivity. In ad-

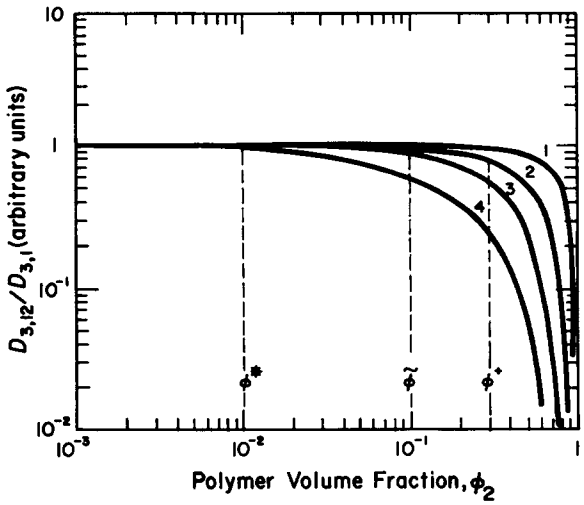

Fig. 8. The effect of the equilibrium polymer volume fraction ϕ_2 on the normalized solute diffusivity in hydrogels when $r = 0.1\xi$ (1), 0.2ξ (2), 0.3ξ (3), and 0.4ξ (4). Experimental data are available between $\phi_2 = 5 \times 10^{-2}$ and $\phi_2 = 7 \times 10^{-1}$.

dition, the result of increasing the size of the solute is a decrease of the solute diffusivity at lower polymer concentrations. It is apparent that the dramatic decrease in the diffusivity occurs as the result of (i) size screening as illustrated by the effect of increase of the solute size and (ii) free-volume availability as illustrated by the effect of an increase of the polymer volume fraction.

The ability of scaling laws to illustrate trends from relatively simple logical arguments imparts their predictive value. The experimentalist would use them as a semitheoretical correlation for data. The omitted constants for eq. (21) are a function of the polymer–solvent pair. Once they are determined for a gel and a solute by experimentally obtaining at least two data points, one can predict the effect of (i) increasing the solute size by a known factor and (ii) increasing the polymer crosslinking by a known amount on the solute diffusivity and rate of release. Equation (21) has been verified by the appropriate data available up to 1987 for solutes smaller than the mesh size, and for equilibrium polymer volume fractions between 0.05 and 0.74.

CONCLUSIONS

Scaling concepts have been shown to be quite useful in the investigation of solute diffusion through hydrogels. The derived scaling laws explain the effects of gel morphology and solute size on the kinetics and mechanism of solute release from hydrogels. The scaling law for the solute diffusivity through a hydrogel has been verified by the data available to date. The model can be used to predict the effects of changing the solute size, degree of crosslinking, and the equilibrium volume degree of swelling for polymer–solvent pairs. This scaling law has two undetermined constants for any gel. Unfortunately, many investigators neglect to characterize gels by the average mesh size and equilibrium volume degree of swelling. These quantities are easily determinable and have been shown to offer significant contributions to the solute release kinetics.

This work was supported by Grant No. CPE-82-07381 from the National Science Foundation.

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Received September 1, 1987
Accepted October 26, 1987