Hindered Diffusion of Dextran and Polyethylene Glycol in Porous Membranes

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The effective diffusion coefficients of dextran and polyethylene glycol in track-etched polycarbonate membranes were measured using membranes with nominal pore sizes of $0.03 \ \mu$ m, $0.05 \ \mu$ m, and $0.1 \ \mu$ m. Experiments were performed using narrow-size range fractions of each polymer. When the Stokes-Einstein radius was used to describe solute size, the observed diffusivities for both polymers agreed closely and were larger than values predicted for rigid spheres, as well as for linear polymers when only steric interactions with the pore wall are assumed. These observations cannot be explained by considering electrostatic interactions between the solute and the pore wall, or solute adsorption on the pore wall. The experimentally measured diffusion coefficients agreed well with a model that treats the polymeric solutes as rigid spheres and includes van der Waals attractive interactions between the solute and the pore wall.

Introduction

When the size of a solute is comparable to the pore size through which it is diffusing, the effective diffusion coefficient of a solute within a pore is usually found to be less than its value in bulk solution. This phenomenon is known as hindered diffusion. An understanding of the equilibrium and transport properties of macromolecules in porous media is important in the design of controlled release devices for the delivery of drugs and pesticides, in dialysis and other membrane separations, in chromatographic separations, and in heterogeneous catalysis.

Efforts to understand the phenomenon controlling hindered diffusion have been ongoing for several decades. A review article by Deen (1987) summarizes much of the theoretical and experimental research in this field. Useful discussions of the hydrodynamic treatment of diffusion in porous media are those of Bean (1972), Anderson and Quinn (1974), Brenner and Gaydos (1977), Malone and Anderson (1978), and Davidson and Deen (1988a). In general, the membrane is treated as an array of cylindrical pores and the solute is assumed to have both Brownian and hydrodynamic characteristics. For spherical solutes in bulk solution, this leads to the Stokes-Einstein equation

$$D_{\infty} = \frac{k_B T}{f_{\infty}} = \frac{k_{\beta} T}{6\pi\mu r_s}$$
(1)

where D_{∞} is the bulk solution diffusion coefficient (cm²/s), k_B is Boltzmann's constant (1.38×10⁻¹⁶ J/k), *T* is absolute temperature (K), f_{∞} is the molecular friction coefficient in bulk solution (kg/s), μ is the solvent viscosity (N·s/m²), and r_s is the radius of the solute (cm).

The reduced solute diffusivity that is typically observed with macromolecular solutes in porous media results from two phenomena. One is thermodynamic and leads to an intrapore concentration driving force, which is less than the driving force based on bulk solution concentrations. Steric, and, in some cases, long-range, interactions between solute and the pore wall exclude the solute from the region near the pore wall. This is described with an equilibrium partition coefficient $K_{\rm eq}$, which is the ratio of the average solute concentration within the pore to that in bulk solution at equilibrium. For a spherical solute in a cylindrical pore

$$K_{\rm eq}(\lambda) = \frac{\int_0^{1-\lambda} e^{-E(\beta)/k_B T} \beta \, d\beta}{\int_0^1 \beta \, d\beta}$$
(2)

where λ is the ratio of solute to pore size (r_s/r_p) , β is the dimensionless radial position of the solute in the pore (r/r_p) , and *E* is the interaction energy between the solute and the pore wall (J).

The second effect is a transport effect. Because of the proximity of the pore wall, the hydrodynamic drag experi-

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enced by the solute in the pore is greater than the drag experienced in an unbounded fluid. This enhanced drag is characterized by K^{-1} , which is the ratio of the friction coefficient of the solute in the bulk solution to that within the pore

$$K^{-1}(\lambda) = \frac{\int_0^{1-\lambda} [f_{\infty}/f(\lambda,\beta)] e^{-E(\beta)/k_B T} \beta d\beta}{\int_0^{1-\lambda} e^{-E(\beta)/k_B T} \beta d\beta}$$
(3)

where $f(\lambda, \beta)$ is the molecular friction coefficient of solute of size λ at position β in the pore (kg/s).

These two effects are combined to define the effective diffusion coefficient D (cm²/s)

$$\frac{D(\lambda)}{D_{\infty}} = K_{\rm eq} K^{-1} \tag{4}$$

An important special case for a rigid spherical solute occurs when only steric interactions are present between the solute and the pore wall (E=0), leading to $K_{eq} = (1 - \lambda)^2$. Combining this with the assumption that $f(\lambda,0)$ adequately approximates $f(\lambda,\beta)$ leads to the commonly used Renkin equation (Renkin, 1954)

$$D = D_{\infty} (1 - \lambda)^2 (1 - 2.104\lambda + 2.089\lambda^3 - 0.948\lambda^5)$$
 (5)

A more exact expression was derived by Brenner and Gaydos (1977) using an asymptotic matching technique to obtain $f(\lambda,\beta)$

$$D = D_{\infty} \left[1 + \left(\frac{9}{8}\right) \lambda \ln \lambda - 1.54\lambda + O(\lambda) \right]$$
 (6)

Values of D/D_{∞} predicted from Eq. 5 are in very good agreement with values predicted using Eq. 6 when $\lambda < 0.1$. A number of experimental investigations have confirmed the validity of Eq. 5 for solutes that are generally rigid and spherical (Beck and Schultz, 1972; Malone and Anderson, 1978; Deen et al., 1981; Baltus and Anderson, 1983; Bohrer et al., 1984; Davidson and Deen, 1988b).

In one of the earliest theoretical studies of the equilibrium partitioning of flexible macromolecules, Casassa (1967) derived expressions for random-flight polymer chains and calculated partition coefficients using a mathematical analogy to transient heat conduction. Casassa and Tagami (1969) extended the earlier work of Casassa to star-branched, random-flight chains. Davidson et al. (1987) used Monte Carlo simulations to calculate partition coefficients for flexible polymers, including the effect of attractive interactions between chain segments and the pore wall in their model. Results showed that small, attractive interaction energies between chain segments and the pore wall produced dramatic increases in the partition coefficient of chains with finite length. Davidson and Deen (1990) performed the analogous continuum "diffusion equation" calculation for the partition coefficient adding an attractive square well interaction. Lin and Deen (1990) used a "diffusion-reaction" equation to describe the effects of long-range polymer-pore wall interactions on the equilibrium partitioning coefficient. Results were presented for square-well potentials, electrostatic doublelayer potentials, and van der Waals potentials.

The intrapore hydrodynamic resistance for flexible polymers has been presented by Davidson and Deen (1988a). The hydrodynamic resistance for a flexible polymer is predicted to be less than that of a rigid sphere with the same λ , when the Stokes-Einstein radius is used to characterize the size of the flexible polymer. However, the effective diffusion coefficient is predicted to be smaller for a flexible macromolecule than for a rigid sphere because the equilibrium partition coefficient is sufficiently smaller for the flexible molecule.

Experimental investigations with flexible macromolecules have yielded mixed results. Diffusion coefficient values of linear polystyrene measured in Nuclepore polycarbonate membranes by Cannell and Rondelez (1980), and in porous mica membranes by Kathawalla and Anderson (1988), were in close agreement with the theory of Davidson and Deen (1988a) for random coil polymers. Bohrer et al. (1984) measured the diffusion rates of the polysaccharides dextran and ficoll as a function of pore size using Nuclepore polycarbonate membranes. Their results for dextran showed transport rates greater than those predicted by either the Renkin equation or the Davidson and Deen theory. Their results for ficoll were in agreement with the Renkin equation, indicating that ficoll behaves more as a rigid sphere than a flexible chain. A later study by Davidson and Deen (1988b) also showed large diffusivities for dextran and polyethylene glycol than those predicted for either spherical solutes or random coil polymers. Diffusion coefficient values for polyisoprene measured by Bohrer et al. (1987) and for poly(ethylene oxide) and poly(vinylpyrrolidone) measured by Davidson and Deen (1988b) were also larger than values predicted from the theory of Davidson and Deen (1988a).

In our laboratory, a study of the effect of solute concentration on hindered diffusion has been undertaken and the results from that study will be reported in a subsequent publication (Shao and Baltus, 2000). In order to interpret transport measurements at a high concentration, an accurate prediction of solute diffusion at low concentration conditions is needed. The objective of the study reported here was to measure the effective diffusion coefficient of narrow-size range fractions of dextran and polyethylene glycol in track-etched polycarbonate membranes under infinite dilution conditions. The measured diffusivity values are compared to those predicted from established models, as well as to those from previously reported experimental measurements. A model is proposed to explain the experimental results.

Experimental

Membranes

Track-etched Nuclepore polycarbonate membranes with a nominal pore radii of 0.1 μ m, 0.05 μ m, and 0.03 μ m were obtained from Corning Separation Division (Corning Costar, Acton, MA). These membranes contain straight, uniform, cylindrical pores. The pore density and pore length were determined by scanning electron microscopy (SEM) using a JEOL JSM-6300 scanning electron microscope. Four membranes were randomly chosen from a given lot, and six differ-

ent regions of each membrane were photographed in order to calculate the average values. The pore density for each membrane was determined by counting the number of pores in surface micrographs of a known area at $16,000-30,000 \times$ magnification. Each photograph contained 50-150 pores. The pore length was determined by measuring the thickness of a cross section. To do this, a piece of the membrane was embedded in paraffin and then sectioned using a microtome (Reichert-Jung, 820). Since pores in the membrane are essentially uniform cylinders, pore length is very nearly equal to membrane thickness, exceeding the membrane thickness only to the extent that the pores are not aligned to the membrane surface. The manufacturer states that the maximum deviation from the normal is 29°. Assuming that all deviations from 0 to 29° are equally probable, the average pore length exceeds the membrane thickness by 6.8% and all calculations employed this factor.

The pore radius was measured using water flow measurements. For a membrane containing cylindrical pores, the Hagen-Poiseuille equation can be used to relate the flow rate (Q) (m³/s) through the pores and the pressure drop (ΔP) across the membrane (Pa)

$$Q = \frac{n\pi \langle r_p^4 \rangle}{8\mu \,\ell} \Delta P \tag{7}$$

where *n* is the number of pores and ℓ is the pore length (cm). The notation $\langle r_p^4 \rangle$ indicates an average over all the pores. By measuring the pressure drop across the membrane at various flow rates, the average pore radius (cm) $\langle r_p^4 \rangle^{1/4}$ was determined from the slope of a plot of Q vs. ΔP . The experiments were performed using a glass diffusion cell. Details of the diffusion cell and the water flow measurement are described elsewhere (Shao, 2000).

Polymer solutes

Dextran T40 was obtained from Pharmacia (Piscataway, NJ) with weight-average molecular weight of approximately 40,000 g/mol and $\overline{M}_w/\overline{M}_n \approx 1.5$. Because hindered diffusion rates are sensitive to solute size, the polydispersity of the polymer sample can have a significant effect on observed diffusivities. Dextran T40 was fractionated on a preparative Superdex 200 pg gel column (16 mm I.D.×600 mm, Pharmacia) to obtain narrow molecular weight distribution samples. For each run, 2 mL of a 100 mg/mL T40 dextran sample in 0.02 M ammonium acetate was injected into the column. The same buffer was used as the eluent, which was pumped at a flow rate of 0.8 mL/min. Four dextran fractions (each about 10 mL) were automatically collected. Each fraction was then desalted and concentrated using Centriprep concentrators (Amicon). Finally, the desalted and concentrated dextran samples were extensively freeze-dried to remove residual water. Each dextran fraction was analyzed using analytical gel permeation chromatography (GPC) with a Shodex OHpak KB-80M gel column (8 mm I.D.×300 mm, Waters) (Shao, 2000). The number and weight average molecular weight of each fraction was determined from the resulting chromatogram using ASTM Standard Method D 3536-91. The ratio $\overline{M}_w/\overline{M}_n$ for each fraction was less than 1.2.



Figure 1. Experimental system used to perform solute diffusion experiments.

Polyethylene glycol (PEG) with a weight-average molecular weight of 10,890 was obtained from Pressure Chemical (Pittsburgh, PA). The manufacturer reported polydispersity of this sample was 1.19. This polymer was used as received without further fractionation.

The bulk phase diffusivity of dextran in water at 25° C was determined using a dynamic light scattering system (Brookhaven Inc.). The incident light wavelength was 514.5 nm, and the scattering was observed at 90°. The photocount autocorrelation function was obtained using a BI 2030 AT correlator. For these measurements, dextran solutions were prepared with concentration less than 5 mg/mL to avoid interactions between dextran molecules.

Hindered diffusion measurements

The diffusion experiments were performed using a glass diaphragm diffusion cell that is described in detail elsewhere (Shao, 2000). It consists of two half-cells, one with a volume of 12.64 cm³, and the other with a volume of 15.87 cm³. The membrane, supported by a stainless steel screen support, was sandwiched between the two half cells. The cell was stirred internally by Teflon coated bar magnets, which were acted upon by a magnet external to the cell. The stirring speed of the external magnet was controlled by a DC motor speed controller (Bodine Electric Company). The diffusion cell was jacketed for water circulation to maintain a constant temperature $(25.0 \pm 0.1^{\circ}C)$. The procedure used for the diffusion experiments is shown in Figure 1. Initially, one-half cell was filled with water (low concentration side), while the opposite cell was filled with polymer solution of known concentration (0.2-0.4 mg/mL). Water was pumped at a constant flow rate through the low concentration cell using a syringe pump. Discrete samples, each with a volume of about 3 mL, were collected from the effluent and were analyzed for solute concentration using a Waters 410 differential refractometer. The time required for each diffusion experiment varied between 7 and 50 h depending on the relative size of the solute and pores. Assuming perfect mixing in each half cell, the measured sample concentration was related to the mass-transfer coefficient (k) (mL/h) using a mass balance written on the sampled reservoir

$$\frac{C_m}{C_H^o} = \frac{kq}{V_L V_m (r_1 - r_2)} \int_{V_{t-1}/q}^{V_{t}/q} (e^{r_1 t} - e^{r_2 t}) dt$$
(8)

$$=\frac{-\left(\frac{k+q}{V_{L}}+\frac{k}{V_{H}}\right)\pm\sqrt{\left(\frac{k+q}{V_{L}}\right)^{2}+\left(\frac{k}{V_{H}}\right)^{2}-\frac{2k(k-q)}{V_{L}V_{H}}}{2}$$
(9)

where C_m is the solute concentration of the *i*th sample, C_H^o is the initial solute concentration in the high concentration cell, V_L is the volume of the low concentration cell, V_H is the volume of the high concentration cell, V_m is the volume of the *i*th sample, V_t is the total volume collected up to and including the *i*th sample, V_{t-1} is the volume collected up to the *i*th sample, and *q* is the flow rate through the low concentration cell. A best fit value for k was determined using a fitting procedure that involved minimization of the function $\sum (C_{m,\text{pred}} - C_{m,\text{meas}})^2$, where $C_{m,\text{pred}}$ is the sample concentration predicted with a given value for k, $C_{m,\text{meas}}$ is the measured sample concentration, and the summation was performed over all collected samples. In Eqs. 8 and 9, all volumes are in mL and all concentrations are in mg/mL. By assuming negligible boundary layer resistances, the effective diffusion coefficient of the polymer in the pore was determined from the measured value of k with the following relationship

$$k = \frac{n\pi r_p^2 D}{\ell} \tag{10}$$

The validity of the assumptions of perfect mixing and negligible boundary layer resistances were verifed experimentally (Shao, 2000). For each membrane, water flow measurements were performed before and after each diffusion experiment to monitor any change in the pore radius.

Results

The pore length and pore density obtained from SEM images of the three different pore size membranes are summarized in Table 1. The values are compared to the nominal values provided by the manufacturer. The values determined from our measurements were used for all subsequent calculations. For each pore size, all membranes came from the same lot.

Table 1. Comparison of Pore Length and Pore Density of Nuclepore Membranes Determined from SEM to Nominal Values Provided by Corning*

| Nominal Size (µm) | Method | Pore Length (µm) | Pore Density (Pores/cm ² $\times 10^{-8}$) |
|-----------------------|----------------|------------------------------|--|
| 0.1 | SEM Corning | $5.80 \pm 0.44 \\ 6.41^{**}$ | $\frac{3.28\pm0.25}{3}$ |
| 0.05 | SEM Corning | $5.81 \pm 0.43 \\ 6.41^{**}$ | $5.66 \pm 0.54 \\ 6$ |
| 0.03 | SEM Corning | $5.95 \pm 0.44 \\ 6.41^{**}$ | $5.35 \pm 0.43 \\ 6$ |

^{*}Reported errors are the 95% confidence limits obtained from images of 4 different membranes.

**The thickness reported by the manufacturer is 6 μ m; the pore length was assumed to be 1.068×thickness.

Table 2. Properties of Polymer Solutes*

| Solute | $\overline{M}_{\scriptscriptstyle W}$ | \overline{M}_n | $rac{\overline{M}_w}{\overline{M}_n}$ | $D_{\infty}^{\dagger}^{\dagger}$ (cm ² /s×10 ⁷) | r_s^{\dagger} (nm) |
|--|--|--|--|---|---------------------------------|
| Dextran T40 F(1) F(2) F(3) F(4) | 37,100 62,600 39,600 26,300 16,600 | 26,000 52,700 37,000 23,400 13,600 | 1.43 1.19 1.07 1.12 1.22 | 4.6 3.6 4.5 5.4 6.8 | 5.3 6.8 5.4 4.5 3.6 |
| PEG | 10,890 | 9,150 | 1.19 | 8.2 | 3.0 |

*T40 is the original sample from Pharmacia; F(1), F(2), F(3) and F(4) are fractions collected using gel permeation chromatography. [†]Obtained from light scattering.

[‡]Stokes-Einstein radius determined from D_{∞} and Eq. 1.

In addition to water flow measurements, the pore radius of several membranes was also determined by measuring the rate of glucose diffusion. The experimental procedure for these measurements was the same as that described for the polymer diffusion experiments. Because glucose is small, bulk phase diffusivity can be assumed in the pores. The pore radius was determined from the measured value of k using Eq. 10 and a literature value for D_{∞} [0.67×10⁻⁵ cm²/s at 25°C, (David, 1994)]. The pore radius values determined from water flow and glucose diffusion were in good agreement, indi-

Characteristics of the original T40 dextran sample and the four fractions obtained from this sample are presented in Table 2. The following relationship between D_{∞} and \overline{M}_{w} was obtained for dextran in water at 25°C

cating that the pore-size distribution in these membranes is

$$D_{\infty} = 7.58 \times 10^{-5} \overline{M}_{w}^{-0.485} \qquad \text{cm}^2/\text{s} \tag{11}$$

The bulk diffusivity of polyethylene glycol in water at 25°C was predicted using the following equation (Singh et al., 1998)

$$D_{\infty} = 1.465 \times 10^{-4} \overline{M}_{W}^{-0.557} \, \mathrm{cm}^2/\mathrm{s}$$
 (12)

Equations 11 and 12 were used with the Stokes-Einstein equation (Eq. 1) to determine an effective radius r_s for each solute.

The hindered diffusion data for the four dextran fractions and PEG are shown in Table 3. The dimensionless diffusivity values D/D_{co} are plotted as a function of dimensionless solute size λ in Figure 2. The experimental values are also compared to values predicted for a solid, spherical solute using the Renkin equation, as well as to values predicted by the theory developed by Davidson and Deen (1988a) for a flexible, linear polymer. Only steric interactions between the solute and pore wall were considered when making these predictions. In the Davidson and Deen theory, α is a permeability parameter which characterizes the resistance to solvent flow through the macromolecule. The prediction presented in Figure 2 was obtained using $\alpha = 34$. It has been shown that the predicted diffusion coefficient is relatively insensitive to α when $34 \le \alpha \le 60$ and that $\alpha = 40$ is an appropriate value for dextran (Davidson and Deen, 1998b). It is apparent from Figure 2 that the experimentally determined hindered diffusion coefficients for both solutes are in good agreement and are larger than those predicted by either the Renkin

narrow.

| | $\langle r_n^4 \rangle^{1/4} *$ | Δr_n^{**} | λ | D | |
|---------|---------------------------------|--------------------|---|---|----------------|
| Solute | $(\mu m)^{\circ}$ | $(\mu \mathbf{m})$ | $(r_s / \langle r_p^4 \rangle^{1/4}_{avg})$ | $(\mathrm{cm}^2/\mathrm{s}\times 10^7)$ | D/D_{∞} |
| Dextran | 0.0885 | -0.002 | 0.08 | 3.3 ± 0.2 | 0.91 |
| F(1) | 0.0535 | -0.0004 | 0.13 | 2.7 ± 0.2 | 0.75 |
| | 0.0324 | -0.0001 | 0.21 | 1.9 ± 0.1 | 0.53 |
| Dextran | 0.0887 | -0.002 | 0.06 | 4.3 ± 0.2 | 0.95 |
| F(2) | 0.0516 | -0.0013 | 0.11 | 3.3 ± 0.2 | 0.73 |
| | 0.0326 | -0.0002 | 0.17 | 2.7 ± 0.2 | 0.60 |
| Dextran | 0.0885 | -0.002 | 0.05 | 4.9 ± 0.3 | 0.91 |
| F(3) | 0.0522 | -0.0014 | 0.09 | 4.2 ± 0.3 | 0.78 |
| | 0.0300 | -0.0012 | 0.15 | 3.3 ± 0.2 | 0.61 |
| Dextran | 0.0842 | -0.0037 | 0.04 | 6.1 ± 0.4 | 0.90 |
| F(4) | 0.0521 | -0.0025 | 0.07 | 5.9 ± 0.4 | 0.87 |
| | 0.0310 | -0.001 | 0.12 | 4.9 ± 0.3 | 0.72 |
| PEG | 0.0840 | +0.0001 | 0.04 | 7.4 ± 0.4 | 0.90 |
| | 0.0530 | -0.0002 | 0.06 | 7.0 ± 0.4 | 0.85 |
| | 0.0320 | -0.0008 | 0.09 | 6.7 ± 0.3 | 0.82 |

 Table 3. Membrane Pore Sizes and Measured Diffusion

 Coefficients of Dextrans and PEG

*Average of pore size determined before and after each diffusion measurement using water flow measurements.

**The pore size measured after solute diffusion measurement minus the pore size measured before the solute diffusion measurement.



Figure 2. Dimensionless hindered diffusion coefficient D/D_{∞} as a function of the solute to pore-size ratio λ .

equation or the Davidson and Deen theory. Our measured effective diffusion coefficient values are also in good agreement with those reported by Davidson and Deen (1988b) for dextran, but are larger than those reported by Davidson and Deen (1988b) for PEG.

The pore size of the membrane was measured before and after each polymer diffusion measurement and the change in observed pore size for each experiment is listed in Table 3. Pore sizes were found to decrease, but only slightly. The pore radius changes during each diffusion experiment were less than 3.7 nm. This small change in membrane pore size is an indication that dextran adsorption is insignificant. Similarly small pore-size changes were also observed for the experiments with PEG.



Figure 3. Measured diffusion coefficient in different ionic strength solutions for fraction F(2) dextran.

The same 0.1 μm pore size membrane was used for each experiment.

The bulk phase diffusivity of dextran in different ionic strength solutions $(10^{-2} \text{ M}, 10^{-3} \text{ M} \text{ and } 10^{-4} \text{ M KCl})$ was determined by dynamic light scattering. The measured values of D_{∞} were essentially the same, indicating that the Stokes-Einstein radius of dextran does not change with solution ionic strength. Hindered diffusion coefficients of dextran were also measured in different ionic strength solutions. The results are presented in Figure 3 and show that the ionic strength of the solution has no effect on the hindered diffusion coefficients. If there were electrostatic interactions between dextran and the pore wall, one would expect the diffusion coefficient to decrease as the ionic strength of the solution decreases. Therefore, it is reasonable to assume that electrostatic interactions between dextran and pore wall are negligible. It was also assumed that electrostatic interactions between PEG (also an uncharged polymer) and the pore wall were negligible.

Discussion

The hindered diffusion coefficients of dextran measured in this study are larger than those predicted using existing theoretical predictions and are in good agreement with values reported by Davidson and Deen (1988b) for dextran in polycarbonate membranes. The measured hindered diffusion coefficients of PEG are in good agreement with the values determined for dextran. Davidson and Deen also measured hindered diffusion coefficients of PEG, but used material with a weight average molecular weight of 21,000, which is about twice as large as the PEG used for our measurements. Because of this difference in the size of the PEG used in the two studies, the range of dimensionless solute size (λ) from the two studies only overlaps slightly. The results do seem to indicate that the values reported from our measurements are larger than the values reported by them. It is possible that this difference may be attributed to different polymer conformations experienced because of differences in the molecular weight of the two polymers. In their study, Davidson and

Deen found significant adsorption of PEG on the pore wall, as indicated by changes in pore size. Our results showed minimal change in pore size during a PEG diffusion experiment, indicating insignificant adsorption of PEG. Therefore, it is also possible that the difference in diffusion coefficients measured in the two studies might be due to different extents of adsorption. The PEG used by Davidson and Deen was obtained from Toyo Soda (Varian Associates, Sunnyvale, CA), while the PEG used for our study was obtained from Pressure Chemical (Pittsburgh, PA). A possible explanation for the difference in apparent adsorption of PEG from the two studies is some difference in chemistry arising from differences in preparation procedure or purification of the polymers.

Attractive polymer-pore interactions could be responsible for the observed increase in effective diffusion coefficients relative to those predicted from models that do not include these long-range interactions. Davidson et al. (1987) considered attractive interactions between the chain segments of the polymer and the pore wall by means of a square-well potential in a region of thickness d_E adjacent to the pore wall. The chain was regarded as having n+1 mass points connected by its *n* segments. Each mass point within the square well was assumed to have an energy $\epsilon k_B T$. They applied a partitioning model using Monte Carlo simulations which incorporated this attractive potential in combination with the hydrodynamic calculations for a noninteracting random coil. Their experimental results fit the model when a moderate interaction energy (ϵ) of 0.26 was used for dextran and 0.20 was used for PEG. In their model calculations, the interaction distance d_E was set equal to the chain segment length. They found that the partition coefficient values predicted using this approach were extremely sensitive to the thickness of the interaction region and suggested that any conclusions based on these calculations should be made with caution.

In this study, we have used an alternative approach to incorporate attractive interactions between the solute and the pore wall on predictions of the partition coefficient. Here, we assume that there are van der Waals interactions between solutes and the pore wall which result in an increase in the partition coefficient and, hence, a corresponding increase in the effective diffusion coefficients in the pore relative to those predicted without long-range interactions. The dextran and the PEG were modeled as solid spheres. A semianalytical result for the van der Waals interactions between a spherical particle and a cylindrical pore surface has been reported (Bhattacharjee and Sharma, 1995). These results show that, for relatively small particles ($\lambda < 0.2$), a simpler model for a sphere interacting with a flat plate provides a reasonable estimate of the interaction force between a sphere and a cylindrical surface. Because $\lambda < 0.2$ for all of our experiments, we have used the simpler flat plate model to describe the attractive interaction between solute and pore wall. The attractive interaction energy for this geometry was given by Hamaker (1937)

$$E(x) = \frac{A}{12} \left\{ \frac{1}{x} + \frac{1}{x+1} + 2\ln\frac{x}{x+1} \right\}$$
(13)

$$x = \frac{h}{2r_s} = \frac{1 - \beta - \lambda}{2\lambda} \tag{14}$$

where A is the Hamaker constant (J) between the solute and polycarbonate membrane in water and h is the distance between the particle surface and the pore wall (cm). Substituting Eq. 14 into Eq. 13 yields the following expression for the interaction energy between the solute at position β and the pore wall

$$E(\beta) = \frac{A}{6} \left\{ \frac{\lambda}{1 - \beta - \lambda} + \frac{\lambda}{1 - \beta + \lambda} + \ln \frac{1 - \beta - \lambda}{1 - \beta + \lambda} \right\} (15)$$

As $h \rightarrow 0$, Eq. 15 predicts that the attractive interaction energy $E \rightarrow \infty$. Since dextran and PEG did not adsorb and immobilize on the pore wall, it is assumed that there is a minimum value for h such that the attractive interaction energy does not go beyond some reasonable value. Therefore, the pore is separated into two regions: one away from the pore wall where van der Waals attractive interactions are present and one near the pore wall where only steric interactions are present. A similar approach was taken by Malone and Anderson (1978) in modeling latex diffusion through mica membranes. They chose $h = 0.05r_s$ as the point of separation between these two regions. In our calculations, $h = 0.05r_s$ was also chosen as the demarcation point between steric and van der Waals interactions. An expression for the equilibrium partition coefficient K_{eq} is then obtained

$$K_{\rm eq} = 2 \int_0^{1-1.05\lambda} \exp\left[\left(-E(\beta)/k_BT\right)\right] \beta d\beta + 2 \int_{1-1.05\lambda}^{1-\lambda} \beta d\beta$$
(16)

The second integral represents the region over which only steric interactions (E = 0) are considered. The effective diffusion coefficient was determined by combining the expression for the intrapore diffusivity (the second term in parentheses on the righthand side of Eq. 5) with the value for K_{eq} from Eq. 16.

In the calculation of $E(\beta)$, a value of the Hamaker constant *A* for solute and polycarbonate interaction in water is needed. The Hamaker constant A_{312} for interactions between material 2 and material 3 in medium 1 can be expressed as (Hiemenz and Rajagopalan, 1997)

$$A = A_{312} = \left(A_{33}^{1/2} - A_{11}^{1/2} \right) \left(A_{22}^{1/2} - A_{11}^{1/2} \right)$$
(17)

where A_{11} is the Hamaker constant for interaction between material 1 and material 1 separated by a vacuum and A_{22} and A_{33} are defined in a similar manner. In this study, material 1 is water, material 2 represents dextran or PEG, and material 3 is polycarbonate. The Hamaker constant for water (A_{11}) is 3.51×10^{-20} J (Visser, 1972), and the Hamaker constant for polycarbonate (A_{33}) is 7.0×10^{-20} J (Mitchell and Deen, 1984). Hamaker constant for dextran and PEG are not available. The Hamaker constant for polymers is predicted to range from 6.15×10^{-20} to 6.6×10^{-20} J (Visser, 1972). Assuming that A for dextran and PEG is 6.38×10^{-20} J (the middle value in this range), Eq. 17 predicts $A = 5.0 \times$ 10^{-21} J for interactions between dextran or PEG and polycarbonate in water. The prediction for D obtained using this value for A is shown in Figure 2. A comparison of this prediction to the experimental values shows excellent agreement.

In the interpretation of our data, we have chosen an alternative approach to explaining our results rather than using the modified random coil model used by Davidson and Deen (1988b) to describe their hindered diffusivity values for dextran. As described earlier, the Davidson et al. (1987) partitioning model includes a square well potential between the polymer and the pore wall and requires a number of arbitrary parameters—the number of segments in the polymer chain, the thickness of the square well, and the interaction energy between each segment and the pore wall. By treating the diffusing solutes as rigid spheres, we are able to rely on previously developed theories describing van der Waals attractions between a sphere and a wall, and to utilize literature values for the Hamaker constant for the materials in our systems.

While dextrans may not be spheres, results from light scattering measurements indicate that they are also more compact than ideal random coils (Suzuki et al., 1982). Light scattering measurements with poly(ethylene oxide) have shown that this polymer behaves as a linear random coil for molecular weights as low as 80,000 (Devanand and Selser, 1991). However, the poly(ethylene glycol) used for our measurements had a molecular weight considerably smaller than this (~10,000). It is quite possible that polymer with this low molecular weight may behave much differently in solution than the higher molecular weight material.

Experimental results presented here and those reported by Davidson and Deen (1988b) show that experimental observations for both polymers cannot be explained using either model without some modifications that account for an apparent attractive interaction between the solute and the pore wall. While Davidson and Deen (1988b) chose to use their random coil model modified to include attractive interactions when interpreting their results, our results show that reasonable predictions can also be made by considering an effective sphere and making appropriate modifications to that model to include attractive interactions. In the thesis of Shao, as well as in a subsequent publication, results from our examination of solute concentration effects on hindered diffusion are reported (Shao, 2000; Shao and Baltus, 2000). These results provide further support for the spherical model proposed here that includes van der Waals attractive interactions with $A = 5.0 \times 10^{-21}$ J between the solute and the pore wall.

Conclusions

Measured effective diffusion coefficients of dextran and polyethylene glycol are in good agreement and are larger than those predicted by either the Renkin equation for rigid spheres or by the Davidson and Deen (1988a) model for noninteracting, flexible polymers. The experimental effective diffusion coefficient values of dextran are comparable to those reported by Davidson and Deen (1988b) for dextran. Diffusion coefficient values for PEG are larger than those reported by Davidson and Deen (1988b) for PEG. The experimental results are in good agreement with a model which treats the polymeric solutes as rigid spheres and van der Waals attractive interactions between the solute and the pore wall are included. The value of the Hamaker constant needed to describe the solute-pore wall interactions in the model calculations is in agreement with a value derived from literature values for polymer-polymer and water-water interactions in a vacuum.

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