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Diffusion and Partitioning of Macromolecules Within Finely Porous Glass

Measurements of diffusion and partitioning of nearly monodisperse polystyrene, having molecular weights of from 600 to 670,000, in chloroform and dichloroethane and of two proteins in aqueous solution were made with leached borosilicate glass cubes having a narrow pore size distribution and pore radi of from 2.5 to 47.6 nm. With increasing ratio of molecular to pore size, the partition coefficient for all solutes decreased; the ratio of effective to bulk diffusivity decreased for the proteins but remained constant for polystyrene. This suggests that polystyrene behaved like a free-draining macromolecule under the conditions of this study.

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SCOPE

Two independent phenomena may lead to a reduced rate of solute diffusion in a pore which is of a size comparable to that of the solute molecule. Both arise as a result of the proximity of the pore wall. First, the solute is effectively excluded from a fraction of the pore volume. This leads to equilibrium partitioning wherein the solute concentration inside the pore is less than the bulk concentration outside the pore. Second, the additional hydrodynamic resistance (above that in free solution) hinders the movement of solute molecules through the pore. Equilibrium partitioning and/or restricted diffusion can play an important role in determining the rate of mass transport through finely porous media, such as catalyst pellets, membranes, and gel chromatography supports.

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Theoretical analyses for a variety of solute configurations and porous structures predict that in the absence of preferential solute adsorption the equilibrium partition coefficient decreases as the ratio λ between the molecular size and pore size increases. This trend has been qualitatively confirmed with studies involving relatively rigid and compact biological macromolecules and flexible chain synthetic macromolecules in rigid porous materials and in swollen hydrophilic gels. Theoretical treatments of restricted diffusion have made use of available solutions for the motion of a sphere or ellipsoid in a continuum bounded by walls of well-defined geometry. A decrease in the ratio of effective to bulk diffusivity as λ increases has been observed experimentally in previous studies using low molecular weight solutes, biological macromolecules, or solid particles in rigid porous media with well-defined pore sizes. No previous studies have been reported, however, of the diffusion of flexible chain polymers in such porous materials.

In the present study, we have investigated diffusion of random-coiling polymers in leached borosilicate glass cubes with average pore radii of 2.5 to 27.6 nm and narrow pore size distribution. Effective diffusion coefficients were evaluated by use of transient diffusion measurements, and solute partition coefficients were evaluated from equilibrium data. Measurements were made with ten polystyrene samples of narrow molecular weight distribution with molecular weights ranging from 600 to 670,000. Experiments were also carried out with two proteins, cytochrome C and hemoglobin, for comparison.

CONCLUSIONS AND SIGNIFICANCE

Equilibrium partition coefficients decreased monotonically from unity for all solutes as λ increased, but the magnitude of the coefficients was generally higher than predicted by available theory for partitioning of a rigid sphere or a random coil in pores of circular or slit-like sections. With proteins, the ratio of effective to bulk diffusivity, when normalized by the estimated tortuosity, decreased monotonically from unity with increasing λ, in qualitative agreement with theory. By contrast, a restricted diffusion effect was not observed with polystyrene. Rather, within experimental error the normalized effective diffusivity ratio was independent of λ, although an unexplained effect of the solvent was observed.

The absence of a restricted diffusion effect with random coiling polymers indicates that caution should be used when such molecules are used as probes in studying transport through finely porous media (for example, membranes). Furthermore, the results suggest that, for restricted diffusion, the effective size scale of the polymer is comparable to that of the monomer unit and that solvent penetrates through the domain of the coiled polymer rather freely. This hypothesis that polystyrene behaves as a nearly free-draining macromolecule is in contrast with the view that solvent is largely immobilized within the core of high molecular weight random-coiling molecules and that such molecules behave as rigid spheres of equivalent hydrodynamic radius. Some support for the present conclusion is drawn from a recent analysis of the intrinsic viscosity of flexible polymer chains which incorporates both partial hydrodynamic interaction and excluded volume effects.

BACKGROUND

Theoretical treatments and experimental studies of equilibrium partitioning of solutes in pores of comparable dimensions have, for the most part, proceeded independently of the phenomena of restricted diffusion. For the case of a rigid sphere in pores of well-defined geometry, simple geometric arguments lead to

$$K_p = (1 - \lambda)^n \tag{1}$$

where K_p is the equilibrium partition coefficient, λ is the ratio of the sphere radius r_s to the characteristic half-dimension of the pore r_p, and $n = 1$, 2, or 3 for a cavity in the shape of a slit, cylinder, or sphere or cone (Ferry, 1936; Porath, 1963; Squire, 1964; Casassa and Tagami, 1969). Ogston (1958) treated the case of a sphere in a random suspension of fibers, and Giddings et al. (1968) have generalized the analysis by evaluating the loss of statistical or configurational entropy of particles of various shapes in a random porous network. The latter analysis reduces to Equation (1) when the appropriate restrictions are imposed.

Partitioning of flexible polymer chains also arises from a loss of configurational entropy because configurations which intersect the walls of a cavity cannot occur. Cottrell, as cited by Russell (1970), considered the effect of finite concentration on random-coiling polymers and obtained Equation (1) in the limit of infinite dilution. Casassa (1967) and Casassa and Tagami (1969) used a different approach to evaluate the fraction of conformations available to both linear and branched polymer chains defined by cavities of various shapes. For a linear polymer chain following random-flight statistics, they obtained

$$K_p = \frac{8}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} \exp\left[- \frac{(2m+1)^2\pi^2}{4} \lambda^2 \right] \tag{2}$$

for a slit-shaped cavity, and

$$K_p = 4 \sum_{m=1}^{\infty} \frac{1}{\beta_m^2} \exp\,(-\beta_m^2\lambda^2) \tag{3}$$

for a long cylindrical cavity. β_m are roots of $J_0(\beta_m) = 0$, and λ is defined as $<s^2>^{1/2}/r_p$ where $<s^2>^{1/2}$ is the root mean square radius of gyration of the polymer.

Experimental evidence for $K_p < 1$ when $\lambda > 0$ has been obtained in various media with rigid and flexible macromolecules of biological and synthetic origin. A substantial body of data has been obtained by inference from elution volumes in gel chromatography (for example, Ackers, 1964; Laurent and Killander, 1964; Squire, 1964; Cantow and Johnson, 1967; Yau et al., 1968; Yau, 1969).

Direct evidence has been obtained through measurements in static equilibrium experiments (Ackers, 1964; Yau, 1969; Russell, 1970; Colton et al., 1971). However, partition coefficients were found essentially equal to unity in a study with nonabsorbing microsolutes in pores of 1.6 nm average radius (Satterfield et al., 1973).

Restricted diffusion is of hydrodynamic origin and arises from the increased frictional drag on the solute as a result of the proximity of the pore walls. The associated fluid-mechanical problem has been solved for various particle and channel geometries (Happel and Brenner, 1965); and the application of these solutions to restricted diffusion has been reviewed (Bean, 1972; Anderson and Quinn, 1974). The most commonly employed expression for the fractional reduction in solute mobility resulting from the proximity of the pore walls is that derived by Faxen (1923) for the axial sedimentation of a rigid sphere through a continuum bounded by a rigid cylinder. More accurate solutions to the same problem are now available (Haberman and Sayer, 1958; Faxen, 1959; Wang and Skalak, 1969).

Restricted diffusion has been investigated with microsolutes and biological macromolecules in steady state diffusion through biological membranes and hydrophilic gels and dialysis membranes (Friedman and Kraemer, 1930; Pappenheimer et al., 1951; Renkin, 1954; Ackers and Steere, 1962; Stein, 1967; Lakshminarayanaiah, 1969; Colton et al., 1971). While these studies have qualitatively confirmed the phenomenon, uncertainties in the structure of the materials employed preclude their usefulness for quantitative comparison with theory. Recently, studies have been carried out with rigid membranes containing pores of well-defined geometry and size. Using a variety of solutes, Beck and Schultz (1972) obtained reasonable quantitative agreement with the model suggested by Renkin (1954) which incorporated Equation (1) for a cylinder and the estimated increase in frictional resistance of Faxen (1923). However, studies of the diffusion of polystyrene latex particles through microporous membranes (Conlon and Craven, 1972; Uzelac and Cussler, 1970) failed to show quantitative agreement with the same relation.

Several studies have been reported of transient diffusion in finely porous particles. The results of Eagle and Scott (1950) qualitatively suggest restricted diffusion. Diffusivities of organic solutes in zeolites (Satterfield and Katzer, 1971; Satterfield and Cheng, 1972; Moore and Katzer, 1972; Satterfield and Chiu, 1974) are many orders of magnitude lower than bulk values and are greatly influenced by specific interactions between diffusing species and pore walls. In the study of Satterfield et al. (1973), measurements were made with a variety of binary systems of paraffinic and aromatic hydrocarbons and with aqueous solutions of salts and sugars in silica-alumina catalyst beads of 1.6 nm pore radius for which λ ranged from about 0.1 to 0.5. Their results for solutes which showed no preferential adsorption demonstrated greater restricted diffusion than was predicted by available theory and were well correlated by the following simple expression

$$\log_{10}\left[\frac{\tau D_{\text{eff}}}{D_b}\right] = -2.0\lambda \qquad (4)$$

where D_{eff} is the effective diffusivity, D_b is the bulk diffusivity, and τ is the tortuosity.

The objective of this study was to investigate the phenomena of equilibrium partitioning and restricted diffusion of synthetic, random-coiling polymers in a well-characterized finely porous material. Restricted diffusion of such polymers does not appear to have been previously characterized quantitatively, although the equation of Renkin (1954) has been applied to the correlation of polystyrene elution volumes in gel chromatography (Yau, 1969) and to the transport of polyvinylpyrrolidone across the glomerular membrane (Lambert et al., 1972). Random coiling polymers differ from the more compact molecules studied heretofore in that the volume occupied by polymer segments is a very small fraction of the total volume within the domain of the macromolecule. The polymer and porous material used here were selected to provide a wide range of molecule-to-pore size ratios. Two proteins were also included in the study for comparison.

EXPERIMENTAL METHODS

A porous glass prepared by leaching was selected for study because of its narrow pore size distribution, its chemical and mechanical stability in organic solvents and aqueous media, and its rigid and continuous pore structure. It could be cut into a shape usable for diffusion measurements and could be regenerated after each experiment.

Heat-treated borosilicate glass plates, 0.5 cm thick, were supplied in unleached form by Corning Glass Works (Corning, New York). The faces were ground to eliminate any structural change at the surface (skin effect) and the plates were then cut into cubes approximately two mm on each side with a diamond saw. The glass had been heated to a temperature slightly below the melting point to cause segregation into silica-rich and borate-rich microphases (Haller, 1965b), the relative sizes of which were controlled by varying the time-temperature history in the heat treatment (Haller, 1965a).

The porous structure was developed by first leaching out the borate-rich phase with 4N HCL (20 cm^3/g glass) at about 90°C for about twenty hours. This was followed by treatment with 0.8 N NaOH (60 cm^3/initial g of glass), replaced every two hours, at about 20°C, which further opened up the pores. The cubes were next treated with 0.1 N HNO_3 for about four hours at 85°C and then rinsed with distilled water until the *p*H was at least six. During both acid and alkali leaching processes, a symmetric shrinking profile was observed to move towards the center of each cube, and this served as a convenient end-point for terminating the leaching process.

Glass cubes with five different pore sizes were prepared. Volumetric-mean pore radii were determined from mercury porosimetry data (American Instrument Company, Silver Springs, Maryland). Heat treatment conditions and duration of the alkali treatment are shown in Table 1 together with some of the properties of the porous glasses used in the study. The pore size distribution was narrow, with more than 90% of the pore volume of each sample being within 10% of the average pore radius, except for the 2.5-nm sample for which 80% of the pore volume was within 20% of its average pore radius. More than 100 cubes of each pore size were prepared, and the average edge length was measured for each. The standard deviation of the edge length was about 5% of the mean except for the 9.25 nm radius material for which the standard deviation was 8% of the average.

Scanning electron micrographs of the surface of several cubes with the two largest pore sizes showed that the pores have cross sections which include circles, ellipses, rectangular slits, and various irregular configurations. Pore dimensions several-fold larger than that determined by mercury porosimetry, as suggested by Haller (1968), were rare; rather, the pore radii tabulated in Table 1 appeared to be a reasonable characteristic dimension.

In order to minimize solute adsorption by scattered hydroxyl groups on the silica surface (Bohemen et al., 1960; Messing, 1969), the porous glass cubes were reacted with hexamethyl disilazane under vacuum at 120°C to replace the hydroxyl groups by trimethyl silane groups. Further details are given by Lai (1973). The resulting material was highly hydro-

TABLE 1. PROPERTIES OF POROUS GLASS USED IN THIS STUDY

Average pore radius,[b] r_p, nm	Heat treatment history[a]	Total time of alkali treatment, hr.	Pore volume,[b] V_p, cm^3/g	Porosity,[c] θ %	Estimated tortuosity,[d] τ
2.5	6 hr @ 560°C	0	0.135	23.0	4.5
9.25	6 hr @ 560°C	4.0	0.54	54.3	2.9
18.5 (18.0)[a]	12 hr @ 580°C	5.5	1.07 (1.10)[a]	70.2	2.3
23.4	16 hr @ 600°C	8.0	0.62	57.7	3.1
47.6	40 hr @ 630°C	16.0	0.68	59.8	3.5

[a] Data provided by Corning Glass Works.
[b] Calculated from measurements provided by American Instrument Co.
[c] Calculated by assuming density of rigid skeleton is 2.2 gm/cc.
[d] Estimated from diffusion measurements. See Results.

phobic but was wettable with organic solvents. Vials containing the cubes were sealed with paraffin and stored in a desiccator when not in use. The cubes were regenerated after each experiment by pyrolysis at 400°C for one day, after which the surface coating procedure was repeated.

Polystyrene with molecular weights ranging from 600 to 670,000 and with very narrow molecular weight distributions was obtained from Pressure Chemical Company (Pittsburgh, Pennsylvania). The polymers were prepared by an anionic polymerization technique (Altares et al., 1964) which yields atactic polystyrene (Clark, 1974) that assumes a random-coiling conformation in solution. Chloroform and 1,2 dichloroethane (reagent grade), both good solvents for polystyrene, were selected so as to further minimize adsorption. Estimated radii of gyration and bulk diffusion coefficients in the two solvents are tabulated in Table 2 for each of the polystyrene samples studied. Radii of gyration cover about a 50-fold range but differ no more than 10% between the two solvents; bulk diffusion coefficients cover about a 30-fold range but the values in chloroform are uniformly higher because of its lower viscosity. The correlations used for estimating the parameters are given in the Appendix.

TABLE 2. PHYSICAL PROPERTIES OF POLYSTYRENE USED IN THIS STUDY (20°C)

	In chloroform		In 1,2 dichloroethane	
M	$<s^2>^{1/2}$ nm	D_b cm^2/s $\times 10^7$	$<s^2>^{1/2}$ nm	D_b cm^2/s $\times 10^7$
600*	0.62	56.0	0.69	34.9
2,120*	1.28	28.9	1.40	18.5
3,600*	1.74	21.8	1.87	14.3
9,300*	3.02	13.3	3.16	8.90
20,800	4.83	8.71	4.94	5.96
38,000*	6.85	6.35	6.90	4.42
110,000	12.7	4.59	12.4	3.54
200,000	18.0	3.25	17.3	2.54
392,000	26.6	2.20	25.1	1.75
670,000	36.3	1.62	33.8	1.30

* $\overline{M}_{vis}$ by intrinsic viscosity; all others $\overline{M}_w$ by light scattering. In all cases, $\overline{M}_w/\overline{M}_n \leq 1.10$. Molecular weight data supplied by Pressure Chemical Company.

Two proteins were selected for their known structure and diffusivity: cytochrome C ($M = 13{,}700$) from equine heart and human hemoglobin ($M = 66{,}000$), both from Sigma Chemical Corp. (twice recrystallized). Approximate dimensions of the two proteins are 2.5 × 2.5 × 3.2 nm and 5.5 × 5.0 × 6.4 nm (Dickerson and Geis, 1967). Results were correlated in terms of the radius of the smallest cylinder through which each protein can pass without distortion, 1.25 nm for cytochrome C and 2.75 nm for hemoglobin. Measurements were made in phosphate buffer (0.07 molar, pH 7) at reduced temperatures so as to minimize thermal denaturation. Using the data of Sober (1970), and assuming $D\eta/T$ = constant, bulk diffusivities at infinite dilution were estimated to be 9.7×10^{-7} cm^2/s for cytochrome C at 10°C and 4.4×10^{-7} cm^2/s for hemoglobin at 5°C.

The glass cubes reacted with hexamethyl disilazane did not prove satisfactory for measurements with protein solutions. Instead, untreated glass cubes were equilibrated with solutions of the proteins to be studied. Measurements were then carried out with these treated cubes in which the adsorption sites had been previously saturated. Calculations indicated that the amount of protein adsorbed, apparently irreversibly, amounted to a substantial fraction of a monolayer if the adsorbed protein was assumed to lie flat on the surface in its native configuration (Lai, 1973). For purposes of data reduction it was therefore assumed that pore radii were reduced by 2.5 nm for cytochrome C and 6.4 nm for hemoglobin.

Several diffusion measurements were also made with sodium chloride in water to estimate the tortuosity of the porous glass.

Methods

The possibility of preferential solute adsorption was studied with nonporous Vycor powder of a composition (> 96% silica) essentially identical to that of the leached borosilicate glass. Vycor tubing was ground wet in a ball mill to produce a powder (specific surface area 1.7 m^2/g) which was then treated with hexamethyl disilazane. One g samples of powder were then contacted with solutions of each of the polystyrene samples (0.8 mg/cm^3) for a period of one week, and the concentration in the liquid was then analyzed and corrected for evaporation of the solvent as determined by weight loss.

Effective diffusivities were measured by following the fractional approach to equilibrium during the unsteady state diffusion of solute into the porous glass cubes. A quantity of cubes containing 0.5 ml pore volume was placed in a vial, followed by addition of 0.5 ml pure solvent to saturate the cubes. One ml of solution of known concentration was then added, and the vial was sealed and placed in a constant temperature shaker bath (±1°C). Three such vials were prepared for each combination of solute, pore size, and solvent to be studied. Approximate calculations indicated that mass transfer limitations in the external solution were negligible. At specified times, ranging from 3 min. to 4 hr, the vials were opened and the bulk solution removed for concentration measurement. No systematic trend in D_{eff} was observed as fractional approach to equilibrium was varied from 0.2 to 0.9; the average of the three measurements is reported here. The standard deviation averaged 15% of the measured effective diffusion coefficient.

The procedure for diffusion measurement was selected to provide a large bulk concentration change and sufficient volume for measurement while at the same time minimizing the number of cubes required. Several experiments (r_p = 18.5 nm, M = 2,120; 9,300; and 38,000 in chloroform) were also performed in which cubes were saturated with polystyrene solution which was then allowed to diffuse into pure solvent. The results were essentially identical to those obtained with the procedure described above. For equilibrium partition measurements, the same procedure as for diffusion was followed, except that the cubes and solution were placed in a flask, sealed air-tight, and stored in a desiccator for one week or more. The bulk solution was then removed for concentration measurement, and the weight change caused by solvent evaporation (usually less than 8%) was taken into account in equilibrium partition calculations.

All experiments were carried out with an initial bulk solute concentration equal to or less than 0.1% (w/v). From the relations given in the Appendix, the maximum increase in solution viscosity (for $M = 670{,}000$) is estimated to be about 15%. Concentration was measured spectrophotometrically (Spectronic 505, Bausch and Lomb). Absorbance (at 262 nm for polystyrene, 270 nm for cytochrome C, and 275 nm for hemoglobin) was linear over the concentration range utilized, and measurements were reproducible to within 0.5%. However, evaporation of solvent during concentration measurement may have led to a small but persistent systematic error.

Calculations

Transient diffusion in a cube of length $2L$ immersed in a well-stirred bath of finite volume is described by

$$\frac{\partial C_p}{\partial t} = D_{\text{eff}} \left[\frac{\partial^2 C_p}{\partial x^2} + \frac{\partial^2 C_p}{\partial y^2} + \frac{\partial^2 C_p}{\partial z^2} \right] \tag{5}$$

subject to initial conditions $C_p = C_{pi}$ everywhere and $C_b = C_{bi}$; and to boundary conditions of symmetry about the center and of

$$V_b \frac{\partial C_b}{\partial t} = -2D_{\text{eff}}\theta A \left[\left(\frac{\partial C_p}{\partial x} \right)_{x=L} + \left(\frac{\partial C_p}{\partial y} \right)_{y=L} + \left(\frac{\partial C_p}{\partial z} \right)_{z=L} \right] \tag{6}$$

where A is the area of one face and $C_b = C_p/K_p$ at x, y, or $z = L$. The solution for the fractional approach to equilibrium is a function of Dt/L^2, the Fourier number, and $\alpha = V_b/K_pV_p$, the ratio between the volume available to the solute in the bath and in the porous material. Although K_p and θ (or V_p) do not appear explicitly in the differential equation, they do arise in the boundary condition, and knowledge of these parameters is necessary for evaluation of D_{eff}.

Implicit in Equation (5) are the assumptions that no adsorption of solute occurs on the pore surface and that the structure of the porous material is isotropic. Evidence supporting the former assumption is presented below. The latter assumption is believed valid because of the symmetric shrinking profile during leaching as well as a similar pattern in the migration of solvent towards the center of dry leached cubes; because of the continuous and interconnected porous structure demonstrated by Haller (1965b); and because of the random nature of the nucleation sites believed to be responsible for phase segregation in borosilicate glass (Haller, 1965a).

An approximate solution to Equation (5) was obtained by use of the Newman product method (Newman, 1930) and the solution given by Crank (1957) for diffusion from a stirred solution of finite volume into a plane sheet. D_{eff} was then evaluated from the measured fractional approach to equilibrium and known values of t/L^2 and α. This approach is not strictly valid because Equation (6) is not variable separable. However, the solution used in this study was compared with the numerical solution of Ma and Evans (1968) for $\alpha = 2$, the largest value employed experimentally, and the largest error in evaluation of D_{eff} was found to be about 6%. Consideration of all errors involved in the experimental procedure and analysis indicates that the expected error in the estimate of D_{eff} is no greater than ±20%.

RESULTS AND DISCUSSION

Fifteen measurements of polystyrene adsorption onto treated nonporous Vycor powder from solution in chloroform or dichloroethane gave a value of 1.02 ± 0.04 for the ratio between the bulk concentration after a one week equilibration and the concentration at the start of the experiment. This provides strong evidence that no preferential adsorption of polystyrene occurred on the silica walls of the porous glass. In the case of protein solutions, the solute which adsorbed following the initial equilibration did not leach out when the cubes were placed in aqueous solution devoid of protein. We therefore believe that in the subsequent studies the diffusing protein was inert towards the pore walls. The evidence for this contention is, of course, less definitive than that for polystyrene.

Equilibrium Partition Coefficient

Values of the equilibrium partition coefficient K_p for all pore sizes and solutes studied are plotted in Figure 1 as a function of $\lambda = \langle s^2 \rangle^{1/2}/r_p$ for polystyrene and $\lambda = r_s/r_p$ for proteins. Also plotted are the theoretical predictions of Casassa (1967) for slit-like and cylindrical pores and the comparable curves from Equation (1) with $n = 1$ and 2.

For $0 < \lambda < 0.4$, the data scatter between the two theoretical curves of Casassa. However, with increasing values of λ the data decrease less rapidly than predicted by theory, and for $\lambda \gtrsim 0.7$ the experimental values of K_p are higher than predicted by any of the theoretical curves. No systematic differences between solvents are apparent, and the data for proteins ($\lambda < 0.25$) conform well to that for polystyrene; this suggests that both random-coiling chain polymers and more rigid, compact proteins behave in a qualitatively similar manner with regard to equilibrium partitioning. These data are in marked contrast to the absence of partitioning observed in an earlier study with microsolutes (Satterfield et al., 1973).

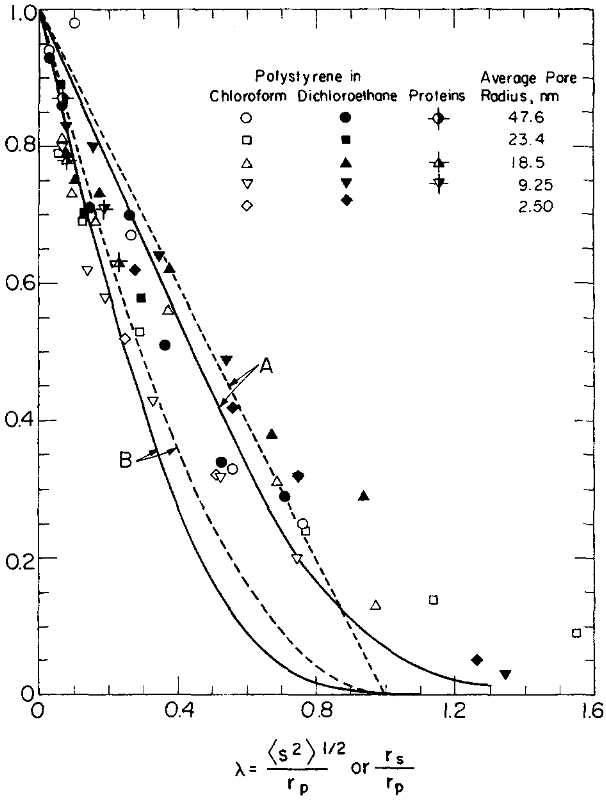

Fig. 1. Dependence of K_p on λ. Dashed curves: Equation (1) with $n = 1$ (A) for a slit and $n = 2$ (B) for a cylinder. Solid curves: Equation (2) for a slit (A) and Equation (3) for a cylinder (B).

The anomalously high values of K_p at high λ may reflect an incorrect assessment of the average pore size. Pore dimensions measured by mercury intrusion are often slightly lower than those found by other methods because the advancing mercury stops at the narrowest section of the pores, and the radii in Table 1 may not properly re-

Table 3. Ratio of Effective to Bulk Diffusion Coefficient, D_{eff}/D_b

Polystyrene molecular weight	Solvent*	Average pore radius, nm 2.5	9.25	18.5	23.4	47.6
600	C	0.22	0.22			
	D	0.17	0.46			
2,120	C	0.17	0.23	0.38	0.42	0.23
	D	0.31	0.48	0.50	0.43	0.31
3,600	C	0.18	0.24	0.42		
	D	0.24		0.62		
9,300	C		0.37	0.36	0.23	
	D		0.47	0.46	0.40	0.33
20,800	C		0.24			0.32
	D		0.45			
38,000	C		0.24	0.42	0.25	
	D		0.40	0.53	0.46	0.38
110,000	C			0.24		0.16
	D			0.33		0.20
200,000	C			0.39	0.18	
	D			0.49		0.33
392,000	C				0.21	0.21
	D					0.34
670,000	C				0.28	0.30
	D					0.33
Polystyrene average		0.22 ± 0.06	0.35 ± 0.11	0.43 ± 0.10	0.32 ± 0.11	0.29 ± 0.07
Cytochrome C			0.16	0.30		
Hemoglobin				0.11		0.27

* C = Chloroform, D = Dichloroethane.

flect the presence of larger regions of the pores which would contribute to a larger K_p. On the other hand, the discrepancy may reflect limitations and inadequacies of the theoretical model. Gaussian statistics underestimate the extension of polymer molecules in space (Debye and Bueche, 1952). Furthermore, excluded volume effects in good solvents such as chloroform and dichloroethane lead to greater expansion of the coil in the periphery than in the core (Kurata and Yamakawa, 1958). The manner by which these effects would influence predicted K_p is not immediately clear. Nevertheless, the data do suggest that the fraction of possible configurations available to flexible chain polymers in cavities is greater than predicted by available theory.

From consideration of the probability of locating the center of mass of one polymer molecule at a specified distance from the center of mass of another molecule, Tanford (1961) suggested that polymer molecules behave much like solid spheres of equivalent radius equal to about 0.85 of the radius of gyration. Multiplication by this factor would clearly shift the data into better accord with theory at high values of λ. However, there does not appear to be a sound theoretical basis for such adjustment of the data.

Effective Diffusion Coefficient

The results of all effective diffusion coefficient measurements are summarized in Table 3. Measurements could not be made in the two runs for which K_p was less than 0.09 because of the very small change in bulk concentration during the course of the run. Despite considerable scatter in the data, several points are apparent. For each solvent-polystyrene molecular weight combination, there is no systematic change in D_{eff}/D_b as pore size is decreased although the magnitude tends to be higher for some pore sizes than for others. Similarly, for each solvent-pore size combination, D_{eff}/D_b does not decrease and, in fact, shows no systematic change with increasing polystyrene molecular weight. The parallel behavior between effective and bulk diffusivities is shown for dichloroethane and several pore sizes in Figure 2. In Table 3 there is, however, a noticeable difference between the data for the two solvents, with D_{eff}/D_b generally higher in dichloroethane than in chloroform.

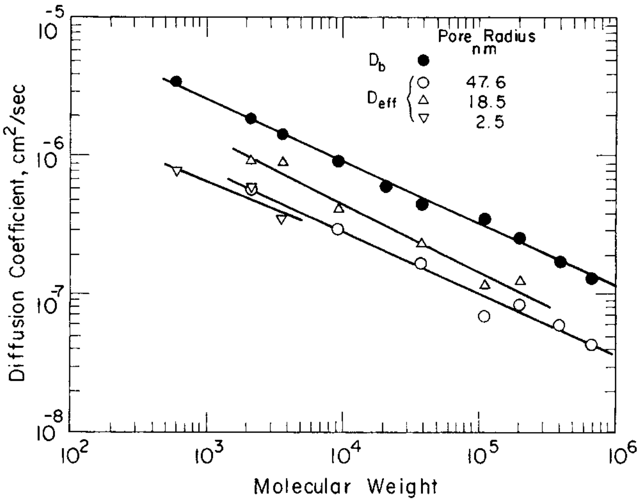

Fig. 2. Dependence of bulk and effective diffusivities on polystyrene molecular weight in dichloroethane (three pore sizes shown). Solid lines are from linear regression analysis of each data set.

D_{eff} in Equation (5) is related to the bulk diffusion coefficient D_b by

$$D_{eff} = \frac{D_b K_r}{\tau} \tag{8}$$

where K_r is the fractional reduction in diffusivity which arises from the increased frictional drag on solute within the pores. The results in Table 3 suggest that for polystyrene K_r is equal to unity or to a constant which varies somewhat with pore size. Neglecting for the moment the differences between results for the two solvents, we assume that $K_r = 1$ and that the reciprocal of the average value of D_{eff}/D_b among all polystyrene data for each pore size provides an estimate of τ (Table 1). The inverse correlation between tortuosity and porosity seems reasonable for a material consisting of random interconnecting pores. The cubes with 2.5 nm pore radii are structurally similar to Vycor porous glass, and the estimated tortuosity of 4.6 lies within the range tabulated by Satterfield (1970) for porous Vycor. Finally, the sodium chloride diffusion measurements gave $D_b/D_{\text{eff}} = 4.7 \pm 0.4$ for the 2.5 nm pore size cubes and 2.3 ± 0.5 for the 47.6 nm pore size cubes. Thus, the values of tortuosity estimated above appear to be reasonable.

The data from Table 3 are shown in Figure 3 where $K_r = D_{\text{eff}}\tau/D_b$ is plotted as a function of λ. The polystyrene data scatter rather widely, but it should be recalled that D_b varies by a factor of about 30. K_r averages 1.00 ± 0.27 for all data and 1.20 ± 0.19 and 0.82 ± 0.19 for the dichloroethane and chloroform data, respectively. The systematic difference between the two solvents is statistically significant; its cause is unknown, although it may result, in part, from uniformly incorrect estimates of bulk diffusion coefficients. In any event, K_r is virtually independent of λ, and restricted diffusion in the conventional sense does not occur for polystyrene in porous glass.

By contrast, K_r for the proteins decreases rapidly with increasing λ, as one would expect for the diffusion of a rigid particle through pores with rigid walls. The reasonable agreement between the protein data and the correlation of Satterfield et al. (1973) may be fortuitous because of uncertainty in the actual thickness of adsorbed protein. Furthermore, the proteins may not be in their native states; for example, there is evidence for dissociation of normally tetrameric hemoglobin into dimers and monomers during permeation across cellulosic membranes (Guidotti and Craig, 1963). There is, nevertheless, an important qualitative difference between the restricted diffusion of the compact and relatively rigid protein molecules and the unrestricted diffusion of polystyrene in the porous glass.

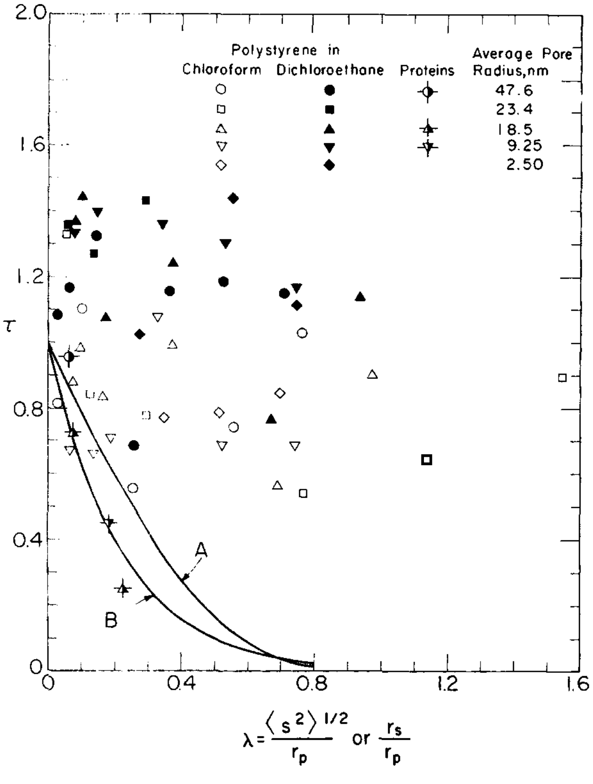

Fig. 3. Dependence of $D_{\text{eff}}\tau/D_b$ on λ. τ evaluated as $(D_b/D_{\text{eff}})_{\text{ave}}$ for each pore size. Curve A: theoretical prediction for a rigid sphere on the axis of a cylindrical channel from Haberman and Sayre (1958). Curve B: empirical correlation of Satterfield et al. (1973).

DISCUSSION

The use of theoretical relations for restricted diffusion appears reasonable for proteins but is clearly not valid for flexible chain polymers. We are aware that flexible chain polymers are sometimes used as probes to study passive transport across biological membranes. Extrapolation of results of such studies to protein transport on the basis of molecular weight or an effective size parameter seems inadvisable. Restricted diffusion of polyethylene glycol has been observed with hydrophilic cellulose membranes (Colton et al., 1971), but the processes operative in such membranes are likely different than in our porous glass (Yasuda et al., 1969); moreover, mutual entanglement between the polymer chains of the diffusing solute and of the membrane may occur as the linear polymer moves in worm-like fashion between the relatively closely-spaced obstacles in a three-dimensional polymeric network (de Gennes, 1971).

The configuration of polystyrene within the pores of the porous glass is unknown. It is conceivable that the polymer chains may to some extent unravel and enter the pores in a largely extended configuration. We view this as statistically unlikely. More probably, the polymer is randomly coiled but constrained to only a fraction of the configurations it can attain in free solution (Casassa, 1967). In either case, the absence of restricted diffusion with increasing λ strongly suggests that the relevant length scale for interaction with the solvent is comparable to that of the individual monomer units (which appear to the fluid as beads on a string) and not to a larger molecular entity as a whole.

It is of interest to compare this conclusion with contemporary concepts of the hydrodynamic behavior and frictional properties of polymer chain molecules in dilute solution. In the free-draining limit the solvent permeates through the polymer chain almost unperturbed by it, and the velocity of the solvent is everywhere nearly the same as though the polymer molecule were not present. At the other extreme is the nonfree-draining, or impermeable, limit wherein the motion of the solvent is markedly altered within the polymer coil. This behavior arises because the peripheral elements of the chain perturb the flow in the neighborhood of the interior elements in such a manner that they are shielded from hydrodynamic interaction with the exterior fluid. Solvent toward the center of the polymer therefore acquires a velocity more nearly that of the molecule itself. This limiting behavior "leads to the concept of an equivalent hydrodynamic sphere, impenetrable to solvent, which would display the same frictional coefficient, or would enhance the viscosity equally, as the actual polymer molecule" (Flory, 1953). Clearly, the results of this study conform more closely to the free-draining limit. We therefore inquire into the behavior of polystyrene in the solvents used in this study, specifically the intrinsic viscosity and the translational diffusion coefficient.

For a free-draining macromolecule, theory predicts $[\eta] \propto M$ and $D \propto M^{-1}$, whereas in the nonfree-draining limit one obtains $[\eta] \propto M^{1/2}$ and $D \propto M^{-1/2}$. Over a wide molecular weight range, however, experimental data invariably follow $[\eta] \propto M^a$ and $D \propto M^{-b}$, where $1/2 \leq a \leq 1$ (Kurata and Stockmayer, 1963) and $0.5 \leq b \leq 0.6$. This behavior has been explained in terms of partial hydrodynamic interaction (for example, Debye and Bueche, 1948; Kirkwood and Riseman, 1948; Peterlin, 1950; Tschoegl, 1963) which leads to a dependence of the Flory-Fox parameter Φ (Flory and Fox, 1951) on molecular weight. Others have contended that the behavior arises from excluded-volume effects (for example, Flory and Fox, 1951; Flory, 1953; Ptitsyn and Eizner, 1960; Ptitsyn, 1962; Kurata and Stockmayer, 1963; Stockmayer and Fixman, 1963) as a result of the molecular weight dependence of the linear expansion factor α and that partial drainage does not occur. The latter hypothesis is reinforced by the fact that $a = \frac{1}{2}$ for all random-coiling polymers at the theta temperature where no net excluded volume effects occur (Kurata and Stockmayer, 1963). Later analyses have taken into account both partial hydrodynamic interaction and excluded volume effects (for example, Kurata and Yamakawa, 1958; Tschoegl, 1964; Yamakawa, 1971).

A limitation of the partial drainage theories is that they predict $[\eta]M^{-1/2}$ and $DM^{1/2}$ should be decreasing functions of molecular weight, whereas they are experimentally found to be constant under theta conditions. That is true for polystyrene down to molecular weights of 500 to 600 (Altares et al., 1964; Rossi et al., 1960). One infers that polystyrene follows nonfree-draining behavior and that the molecular weight dependencies in the solvents of this study (see Appendix) arise primarily from excluded volume effects. In measurements of the dynamic mechanical properties of dilute polystyrene solutions, Frederick et al. (1964) observed a transition from nonfree-draining behavior (Zimm, 1956) to free-draining behavior (Rouse, 1953) with increasing concentration and molecular weight in good solvents. However, the values above which this transition occurred were substantially higher than the conditions of this study. Consequently, there is an apparent paradox between the nonfree-draining behavior of hydrodynamic properties of polystyrene and the free-draining behavior we have observed with respect to restricted diffusion.

Recently, however, Yamakawa (1971) and Osaki (1972) have reexamined some of the basic assumptions upon which all previous treatments of hydrodynamic interaction have been based. They have shown that conditions exist whereby apparent nonfree-draining behavior can occur (that is, $[\eta]M^{-1/2}$ and $DM^{1/2}$ are virtually independent of molecular weight), even though there is in fact only partial hydrodynamic interaction. Tschoegl (1974) has expanded upon Osaki's analysis to include excluded volume effects, and we have used his results to evaluate polystyrene in chloroform and dichloroethane (see Appendix). Of primary interest is the hydrodynamic interaction parameter h, the square root of which is proportional to the ratio between a length scale of the random coil and a length scale characteristic of hydrodynamic shielding; $h = 0$ for a freely permeable coil and $h = \infty$ for an impermeable coil. Over the molecular weight range 9,300 to 670,000 in the two solvents, h is estimated to be roughly of order unity. Consequently, we tentatively conclude that although the hydrodynamic properties of polystyrene display apparent nonfree-draining behavior in chloroform and dichloroethane, there is in reality only limited hydrodynamic interaction and thus significant permeation of solvent through the domain of the coil.

In retrospect, the finding that polystyrene does not undergo restricted diffusion over the range of λ investigated, and the deduction that it therefore behaves more like a free-draining than a nonfree-draining macromolecule, may not be so surprising. Theories of the hydrodynamic properties of polymers in solution are continuing to evolve, and we expect that the observations in this study may eventually be fully reconciled with theory.

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NOTATION

A = area of one face of cube, cm^2
a = exponent in Equation (A3)
B = constant in Equation (A4)
C_b = solute concentration in bulk solution, g/cm^3
C_p = solute concentration in pores, g/cm^3
D = diffusion coefficient, cm^2/s
D_b = diffusion coefficient in bulk solution, cm^2/s
D_{eff} = effective diffusion coefficient in pores, cm^2/s
h = hydrodynamic interaction parameter
$J_0(x)$ = Bessel function of the first kind or order zero
K = coefficient in Equation (A3)
K_p = C_p/C_b, equilibrium partition coefficient
K_r = fractional reduction of diffusivity resulting from proximity of pore wall
L = one-half of cube edge length, cm
M = molecular weight
$\overline{M}_n$ = number-average molecular weight
$\overline{M}_{\text{vis}}$ = viscosity-average molecular weight
$\overline{M}_w$ = weight-average molecular weight
n = exponent in Equation (1)
n_s = effective number of chain segments
r_p = average pore radius, nm
r_s = critical solute molecular radius, nm
$<s^2>^{1/2}$ = root mean square radius of gyration, nm
T = temperature, °K
t = time, s
V_b = bulk (external) solution volume, cm^3
V_p = internal pore volume, cm^3
x, y, z = rectangular coordinates

Greek Letters

α = V_b/K_pV_p, ratio between volume available to solute in bulk solution and volume available in pores
β = free-draining parameter
β_m = roots of $J_0(\beta_m) = 0$
ϵ = excluded volume parameter
η = solvent viscosity, poise
$[\eta]$ = intrinsic viscosity, dl/g
θ = pore volume fraction
λ = $<s^2>^{1/2}/r_p$ or r_s/r_p, ratio of solute radius to pore radius
τ = tortuosity

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APPENDIX: PROPERTIES OF POLYSTYRENE

Light-scattering data for the root mean square end-to-end distance as a function of molecular weight were fitted to a power law function. In terms of the root mean square radius of gyration (in nm), we find

$$\langle s^2\rangle^{1/2} = 0.0150\,M^{0.581} \qquad \text{(A1)}$$

in chloroform (Oth and Desreux, 1954), and

$$\langle s^2\rangle^{1/2} = 0.0201\,M^{0.554} \qquad \text{(A2)}$$

in dichlorethane (Outer et al., 1950). Extrapolation of these relations to the low molecular weight samples may be somewhat unrealistic, but whatever error is incurred should have no bearing on the qualitative conclusions of this study.

Intrinsic viscosity is correlated in terms of the empirical Mark-Houwink relation

$$[\eta] = KM^a \qquad \text{(A3)}$$

In chloroform, $K = 1.12 \times 10^{-4}$ dl/g and $a = 0.73$ (Bawn et al., 1950). In dichlorethane, $K = 2.1 \times 10^{-4}$ dl/g and $a = 0.66$ (Outer et al., 1950). At the theta point, $K = 8.2 \times 10^{-4}$ dl/g and $a = 0.50$ (Kurata and Stockmayer, 1963).

In a study of macromolecule diffusion with five polymer-solvent combinations ($M > 44{,}000$), Tsvetkov and Klenin (1958) found

$$\eta D T^{-1} (M[\eta])^{1/3} = B \qquad \text{(A4)}$$

where B varies slightly from one system to another. For polystyrene in dichloroethane ($\eta = 0.0080$ poise), $B = 3.52 \times 10^{-10}$. At 20°C one obtains

$$D = 2.17 \times 10^{-4}\, M^{-0.553} \qquad \text{(A5)}$$

Meyerhoff (1960) reported $D = 1.84 \times 10^{-7}$ cm^2/s for polystyrene ($M = 540{,}000$) in chloroform ($\eta = 0.0056$ poise) at 20°C. Equation (A4) gives $B = 3.42 \times 10^{-10}$; thus, for chloroform at 20°C

$$D = 3.72 \times 10^{-4}\, M^{-0.577} \qquad \text{(A6)}$$

Equations (A5) and (A6) were used for $M \geqq 110{,}000$. A separate procedure was used for $M \leqq 38{,}000$. The data of Rossi et al. (1960) for diffusion of polystyrene ($550 \leqq M \leqq 34{,}500$) in benzene ($\eta = 0.0065$ poise) at 20°C was fitted by $D = 1.39 \times 10^{-4}\, M^{-0.525}$. Since the Mark-Houwink parameters for benzene and chloroform are identical (Bawn et al., 1950), only a viscosity correction was employed, yielding for chloroform at 20°C

$$D = 1.61 \times 10^{-4}\, M^{-0.525} \qquad \text{(A7)}$$

The diffusivity in dichloroethane was estimated by assuming $D\eta\langle s^2\rangle^{1/2}$ is a constant, independent of solvent or molecular weight, and $\langle s^2\rangle^{1/2}$ was assumed to be the same in benzene and chloroform. The error incurred by these assumptions should be small (Kurata and Stockmayer, 1963). The result for dichloroethane at 20°C is

$$D = 0.843 \times 10^{-4}\, M^{-0.498} \qquad \text{(A8)}$$

The use of two equations for different molecular weight ranges leads to a slight discontinuity in the estimates, as shown in Figure 2.

The hydrodynamic interaction parameter h was evaluated from (Tschoegl, 1974):

$$h = \frac{1}{4}(1-\beta)(1-\epsilon)n_s^{(1-\epsilon)/2} \qquad \text{(A9)}$$

The excluded volume parameter ϵ was obtained from Equations (33) and (36) of Tschoegl (1964), and the free-draining parameter β from Figure 3 of Tschoegl (1974). n_s is the effective number of chain segments, the ends of which are distributed according to Gaussian statistics. Each chain segment was assumed to be composed of 10 monomer units (Flory, 1969), each of molecular weight 52. Over the range $9300 < M < 670{,}000$, ϵ increased from 0.04 to 0.18 in chloroform, with a similar but slightly lower range in dichloroethane, whereas β decreased from 0.6 in chloroform (0.4 in dichloroethane) to 0 ($M \geqq 200{,}000$ in chloroform, $M \geqq 110{,}000$ in dichloroethane). h increased with molecular weight, ranging from about 0.4 to 3.8 in chloroform and 0.8 to 4.4 in dichloroethane.

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