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Restricted Diffusion in Liquids within Fine Pores

The effect on the liquid-phase effective diffusivity in fine pores of the ratio of solute molecular diameter to pore diameter and of preferential solute adsorption was studied by measurements on homogeneous silica-alumina bead catalyst (pore diameter = 3.2 nm). A proposed empirical correlation is based on the investigation of a variety of binary systems of paraffins and aromatic hydrocarbons and of aqueous solutions of sugars.

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SCOPE

The rate of solute diffusion in liquids within finely porous materials becomes observably less than would be expected when the solute molecular size becomes significant with respect to the pore size. Quantitative prediction of the corresponding effective diffusivity can be of importance in guiding experimental work and improving engineering design in such disparate applications as molecular sieve operations, catalytic processing of heavy liquid petroleum fractions, conversion of high molecular weight substrates by immobilized enzymes, gel permeation chromatography, and permeation through natural and synthetic membranes.

Previous work with well-characterized, rigid porous materials include studies with zeolites (Satterfield and Katzer, 1971; Satterfield and Cheng, 1972; Moore and Katzer, 1972) where the pore diameter is of the order of one nm (10Å) and studies with membranes (Beck and Schultz, 1972) with pore diameters of the order of 10 nm (100Å) and greater. The present study examined quantitatively some of the effects of molecular size and physiochemical properties on diffusion in homogeneous silica-alumina catalyst beads having a median pore diameter of 3.2 nm. Effective diffusion coefficients were evaluated by use of transient diffusion measurements, and solute partition and adsorption phenomena were evaluated from equilibrium data. Measurements were made with a large number and variety of binary systems of paraffinic and aromatic hydrocarbons and with aqueous solutions of salts and sugars. The ratio of solute critical molecular diameter (that of the smallest cylinder through which the molecule can pass without distortion) to pore diameter was varied from 0.088 to 0.506.

CONCLUSIONS AND SIGNIFICANCE

The ratio of solute concentration inside pores to concentration outside pores at equilibrium was found to be approximately unity for solutions of saturated hydrocarbons in one another and aqueous solutions of salts and sugars, even when the solute molecules had critical diameters as much as one-half the diameter of the pores. These results are in contrast to theoretical predictions and to previous experimental results obtained with solutions of macromolecules, and they imply the absence of a geometric exclusion effect in the present study. Aromatic hydrocarbons preferentially adsorbed from solution in saturated hydrocarbons, and the magnitude of this effect increased as the number of aromatic rings in the molecule increased.

With nonadsorbing solutes, the logarithm of the ratio of effective to bulk diffusivity decreased linearly with increasing ratio of solute critical molecular diameter to pore diameter, thereby leading to a simple empirical correlation. This behavior does not conform to the prevailing hydrodynamic model for the increased drag on a molecule diffusing in a fine cylindrical pore (Bean, 1972; Beck and Schultz, 1972).

Adsorption further decreased the effective diffusivity below that for an equivalent-sized nonadsorbing solute. An approximate model consistent with the observed data is proposed to describe diffusion occurring in the bulk of the pore and simultaneously in the immediate vicinity of the pore wall with a greatly decreased translation mobility.

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BACKGROUND AND PREVIOUS STUDIES

Consider first the case of steady state diffusion through a porous membrane of thickness h in the absence of convection. Assuming that Fick's first law holds, that the solute diffusion coefficient is independent of concentration, and that specific interactions between solute and porous material are absent, the flux of solute per unit total area can be written

$$J = D_{eff} \Delta C_b / h \tag{1}$$

where D_{eff} is the effective diffusion coefficient when the driving force is the concentration difference beween the solutions on either side of the membrane ΔC_b. D_{eff} is conventionally related to the bulk diffusivity in free solution D_0 by

$$D_{eff} = D_0 \theta K_p K_r / \tau \tag{2}$$

where θ is the pore volume fraction, τ is the tortuosity, K_p is the equilibrium partition coefficient (that is, the ratio of concentration inside the pore to concentration outside the pore at equilibrium), and K_r is the fractional reduction in diffusivity within the pore which results when the solute and pore size are of comparable magnitude.

The concept of an equilibrium partition coefficient was first introduced by Ferry (1936) in terms of a geometric exclusion effect. Since the center of mass of the molecule, assumed to be a hard sphere, cannot be closer to the pore wall than the distance of the molecular radius, Ferry obtained

$$K_p = (1 - \lambda)^2 \tag{3}$$

where λ is the ratio of the molecule diameter to the pore diameter. By similar reasoning, one obtains

$$K_p = \frac{[1 - \lambda_{solute}]^2}{[1 - \lambda_{solvent}]^2} \tag{4}$$

when the size of the solvent molecule is also significant with respect to the pore diameter. Cottrell, as reported by Russell (1970), treated the problem for random coiling polymers by considering the difference between configurational entropy inside the pore and in free solution. He obtained Equation (3) in the limit of infinite dilution. Casassa and Tagami (1969) calculated the fraction of conformations available to a random coiling chain confined by various cavities. Their results for a cylindrical pore differ quantitatively from Equation (3). Experimental evidence for equilibrium partition coefficients less than unity has been obtained in various media with solutions of synthetic and biological macromolecules by direct equilibrium experiments and by inference from elution volumes in gel chromatography (Ackers, 1964; Yau, 1969; Russell, 1970; Colton et al., 1971).

The prevailing explanation for restricted diffusion in pores of small diameter is of fluid dynamic origin. Friedman and Kraemer (1930) first suggested that the reduced diffusivity in fine pores resulted from increased frictional drag on the solute as a result of the proximity of the solid walls, and for a quantitative estimate they employed the first-order solution of Ladenburg (1907) for the axial sedimentation of a hard sphere through a continuum bounded by a rigid cylinder. Pappenheimer et al. (1951) combined this factor with Equation (3) for the partition coefficient. Lane (1950) and Renkin (1953) employed the higher-order solution of Faxen (1922) which is valid up to about $\lambda = 0.5$; this leads to

$$K_p K_r = (1 - \lambda)^2 (1 - 2.104\lambda + 2.09\lambda^3 - 0.95\lambda^5) \tag{5}$$

which is often referred to as the Renkin equation. Bean (1972) recently incorporated the improved result of Bohlin (see Faxen, 1959). Haberman and Sayre (1958) obtained an exact solution to the fluid dynamic problem valid up to $\lambda = 0.8$. These and solutions for other geometries have been reviewed (Happel and Brenner, 1965) and have been verified experimentally in a macroscopic system (Fidleris and Whitmore, 1961).

Equation (5) has been applied to solute diffusion through biological membranes (Stein, 1967) and through swollen hydrophilic membranes, for example, regenerated cellulose (Lakshminarayanaiah, 1969). In the latter, diffusion occurs primarily through amorphous regions of polymeric chains which are in continual random motion and which are held together by impermeable crystalline regions. While data have been fitted reasonably well with Equation (5) (Bean, 1972) the use of an equivalent pore diameter for these materials is clearly a convenient mathematical concept whose relationship to physical reality is unclear. Studies with rigid porous membranes are free of this limitation, but results have been contradictory. Uzelac and Cussler (1970) measured the diffusion of latex spheres (910 nm diameter) through Millipore membranes. The decrease in measured diffusivity as λ increased from about 0.1 to about 0.4 followed that predicted from the model for increased hydrodynamic drag but without inclusion of an equilibrium partition coefficient. Beck and Schultz (1972) studied the diffusion of molecular solutes through thin, etched mica membranes containing straight pores of well-defined geometry and narrow pore size distribution with diameters ranging from 9 to 60 nm. Their data in the range $0 < \lambda < 0.2$ correlated well with Equation (5).

It is desirable to separate the independent phenomena of equilibrium partition and restricted diffusion for a more complete understanding of diffusion through fine pores. This has been done in very few studies (Colton et al., 1971). Separation of these two effects follows naturally from measurements of fractional approach to equilibrium during unsteady state diffusion in porous solids, where the variation of concentration with time is described by

$$\frac{\partial C_p}{\partial t} = D_{eff} \nabla^2 C_p \tag{6}$$

Here, D_{eff} can be expressed by

$$D_{eff} = D_0 K_r / \tau \tag{7}$$

Unlike steady state diffusion through a membrane, neither θ nor K_p enter into this expression. The same is true of the boundary condition at the surface of the porous solid if the surrounding bath volume is effectively infinite. The restricted diffusion phenomena thus may be evaluated directly.

Experimental studies on unsteady state diffusion in finely porous media are limited in number. Eagle and Scott (1950) reported effective diffusivity measurements for toluene diffusing through iso-octane in a variety of finely porous materials with pore diameters ranging from 3 to 9 nm. While the results qualitatively indicated that restricted diffusion occurred, interpretation is difficult because of the lack of tortuosity values and data on the observed effect of preferential toluene adsorption. Satterfield and others (Satterfield and Katzer, 1971; Satterfield and Cheng, 1972; Moore and Katzer 1972) have studied unidirectional and counterdiffusion of organic solutes in zeolites with pore diameters less than one nm ($\lambda \sim 1$). Effective diffusivities many orders of magnitude lower than bulk values have been measured, and it has been found that diffusion rates are greatly influenced by specific interactions between diffusing species and pore walls.

The objective of this study was to further characterize the restricted diffusion phenomenon by transient diffusion experiments. A porous material was selected such that the pore diameter was intermediate between the smallest size studied by Beck and Schultz (1972) and that characteristic of zeolites. Solute-solvent systems were selected to provide a range of molecule-to-pore diameter ratios and to provide the occurrence and absence of preferential solute adsorption.

EXPERIMENT

Materials

The porous material used in this study was homogeneous silica-alumina catalyst beads provided by the Mobil Research and Development Corporation. This material was selected for its small pore diameter, narrow pore size distribution, rigid stucture, and convenient form (3 to 4 mm diameter spheres). The pore size distribution, as determined from mercury porosimetry data provided by Mobil, was narrow with 80% of the pore volume contained in pores between 2.9 and 3.5 nm in diameter. The median pore diameter on a volume basis was taken to be 3.2 nm. Assuming straight cylindrical pores, an average pore diameter of 3.7 nm was estimated from surface area data provided by Mobil (390 m^2/g) and pore volume measurements.

The beads were used as received without additional treatment. They were kept in sealed containers because exposed beads rapidly adsorb foreign matter, as evidenced by discoloration and a gain in weight. The average pore volume was determined experimentally by absorption of an organic liquid (0.355 cm^3/g for 2,2,4-trimethyl pentane or toluene) or water (0.364 cm^3/g). The slightly greater penetration of water may have resulted from its smaller molecular size. The apparent density was 1.22 g/cm^3, and the void fraction was about 0.44. Beads of uniform size and spherical shape with no visible cracks were selected for study.

Solute-solvent systems covering a wide range of molecular size were chosen with several factors in mind. Solutes with no preferential adsorption were necessary to separate the effects of molecular size from those of adsorption. Systems with various degrees of preferential solute adsorption were also studied. Reagent grade chemicals were used whenever possible. Table 1 lists the compounds employed and their molecular weight and critical molecular diameter d_s. The latter quantity is the diameter of the smallest cylinder through which the solute can pass without distortion. The least hindered conformation of each compound was determined by use of molecular models, and the critical diameter was then determined by drawing each molecule to scale using published values for bond lengths, bond angles, and Van der Waals radii (Pitcher, 1972). Critical diameters ranged from 0.28 nm for water to 1.62 nm for cycloheptaamylose. This parameter was found to correlate the diffusion data better than either the solute molal-volume at the normal boiling point or the diameter calculated with the Stokes-Einstein equation from the bulk diffusivity in free solution (Pitcher, 1972). Estimation of the critical diameter in aqueous solution is complicated by the hydration of electrolytes (Robinson and Stokes, 1965) and sugars (Scatchard, 1921). Comparison of the relative volumes of solute and hydrated water molecules suggests that an effect upon effective solute size may be significant only for sodium chloride.

Apparatus and Procedure

The experimental work fell into two principal categories: equilibrium partition measurements and diffusion experiments.

TABLE 1. CRITICAL MOLECULAR DIAMETER OF COMPOUNDS USED IN THIS STUDY

Compound	d_s, nm	Mol. wt.
Water	0.28	18
Sodium chloride	0.28	58
Hexane	0.49	86
1-Octene	0.49	112
n-decane	0.49	142
Hexadecane	0.49	226
Toluene	0.63	92
Cyclohexane	0.65	84
Methyl cyclohexane	0.67	98
2,2,4-trimethyl pentane (iso-octane)	0.67	114
Cumene	0.67	120
m-diisopropyl benzene	0.74	162
1,3,5-trimethyl benzene (mesitylene)	0.84	120
Glucose	0.86	180
o-terphenyl	0.88	230
1,3,5-triethyl benzene	0.92	162
Sucrose	0.93	342
1,3,5-triisopropyl benzene	0.96	204
1,3,5-triisopropyl cyclohexane	1.05	210
1,3,5-triphenyl benzene	1.22	306
Cyclohexaamylose (α-cyclodextrin)	1.47	972
Cycloheptaamylose (β-cyclodextrin)	1.62	1,143

Solute concentration was measured with a differential refractometer (Brice-Phoenix) after calibration with known solutions. Measurements were accurate to within 0.002 wt. % (w/w) in aqueous solution and to within 0.005 wt. % with hydrocarbons. All experiments were carried out at room temperature, 24 ± 2°C, unless otherwise indicated.

Equilibrium concentration inside the pores of the silica-alumina beads was determined by placing a known weight of dry beads in a measured amount of solution of known concentration. After the solution reached equilibrium, the concentration of the solution outside the beads was measured. With pore volume of the beads known, the concentration inside the beads could be calculated by a mass balance. Adsorption of solute was completely reversible.

For diffusion experiments, the beads were initially equilibrated for at least a day with the desired dilute solution (usually less than 5 wt. % concentration). Excess solution was then removed, and the beads were placed in a 500 ml well-stirred bath of pure solvent. The bath volume was larger than the volume of solution in or on the beads by a factor of 300 or more and thus could be treated as infinite. Solute concentration in the bath therefore remained essentially zero throughout a run and was not affected by either the solution entrained on the bead surface (which was quickly washed away) or the solute diffusing out from the pores. The bath was agitated by a magnetic stirrer operated at its maximum speed. This was substantially above the speed at which the measured effective diffusivity became a function of stirrer speed. The absence of significant external mass transfer resistance was also confirmed by approximate calculation (Pitcher, 1972). Bath temperature was measured with a thermometer. Individual runs varied from five minutes to several hours; most were about one hour in duration.

At periodic intervals, a number of beads, usually about 20, were removed from the bath and placed in a small vial containing about one ml solvent. Excess liquid clinging to the beads could be treated as pure solvent. The vial containing beads and solution was weighed and allowed to stand until equilibrium was reached, after which the solute concentration in the external solution in the vial was measured. Together with knowledge of the equilibrium partition coefficient, this permitted calculation of the total solute concentration in the beads and thus the fractional approach to equilibrium at the time of their removal from the bath. Fractional approach to equilibrium at time t is defined here as $(C_{p,t} - C_{p,i})/(C_{p,\infty} - C_{p,i})$, where subscripts i and ∞ refer to conditions at the start of the experiment and after the system has reached equilibrium, respectively. Effective diffusivity was then calculated from the solution to Equation (6) relating fractional approach to equilibrium to $D_{\mathrm{eff}}t/a^2$ for a sphere of initially uniform concentration exposed to a step change in surface concentration (Crank, 1957). Diffusivities were corrected to 25°C by assuming $D_{\mathrm{eff}}\mu/T$ to be constant; this correction usually amounted to less than 5%. The same calculation procedure was used whether solute adsorption did or did not occur. D_{eff} was determined from two to four measurements during a run and showed little or no dependence upon time. Initial solute concentration was varied for most systems, and no significant effect on D_{eff} was observed within the dilute range investigated. The average of several runs is reported here.

The use of a large bath and the removal of individual beads was necessitated by the small quantity of acceptable porous beads available, but the method has an important advantage over the conventional use of a large number of beads in a stirred bath and measurement of bath concentration directly. Excess liquid clinging to the beads on introduction into or removal from the bath is unimportant as long as the mixing is adequate. Since the bath is effectively infinite in volume, the removal of beads or liquids has no effect on the rate of diffusion in the remaining beads.

Diffusion experiments were also performed with the bath initially containing dilute solution and the beads saturated with pure solvent. The diffusivities determined by this method were identical within experimental error to those measured by the technique described above. A few diffusivity measurements were also made by shaking several solvent-saturated beads in a small vial containing a known quantity of solution and observing the concentration change in the external solution.

RESULTS AND DISCUSSION

Equilibrium Studies

The results of the equilibrium partition experiments are shown in Figure 1 where the solute concentration inside the pores is plotted versus the concentration in the external solution for the various systems studied. Square root coordinates are employed to facilitate plotting a wide concentration range. The following groups of binary systems were studied: (1) selected substituted benzenes as solutes in 2, 2, 4-trimethyl pentane, plus a few cases in which 2, 2, 4-trimethyl pentane was the solute; (2) selected pairs of paraffins, including cycloparaffins and one system with 1-octene, and (3) sodium chloride and selected sugars in water. In the dilute concentration range where the diffusion experiments were carried out, the isotherms are all linear and the square of the slope is the experimentally measured value of K_p.

It can be seen that values of K_p do not differ significantly from unity for solute-solvent systems consisting of saturated hydrocarbons (paraffins and cyclohexanes) or aqueous solutions of sugars and sodium chloride. The greater scatter for aqueous solutions probably resulted from slight bead deterioration which changed the solution refractive index. Values of K_p equal to unity are not surprising for small solute molecules which are comparable in size to solvent molecules. However, the bulk of the data is clearly inconsistent with the predictions of Equations (3) or (4), particularly for the aqueous solutions of the largest sugars which have critical diameters of about 1.5 to 1.6 nm. For example, Equation (4) predicts $K_p \sim 0.3$ for an aqueous solution of cycloheptaamylose in 3.2 nm diameter pores in contrast to the experimental value of about unity.

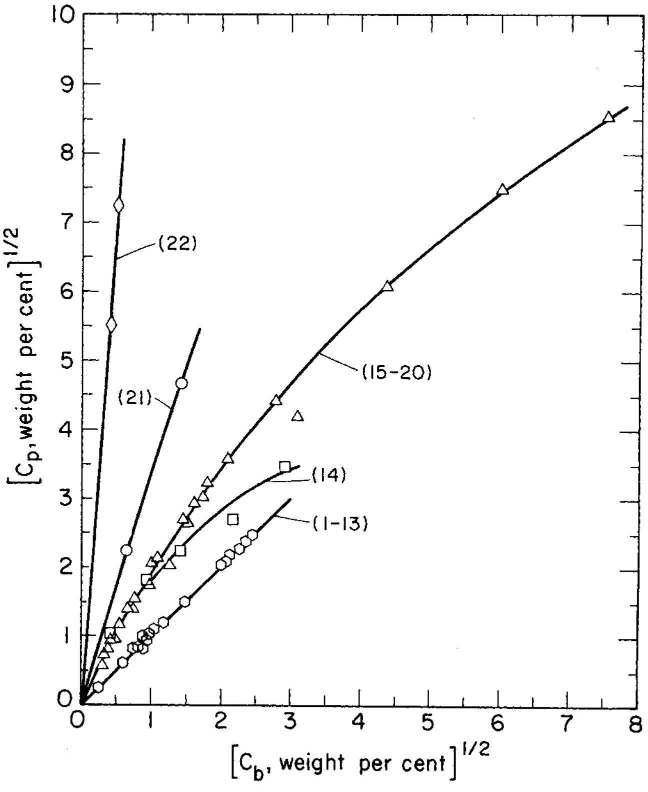

Fig. 1. Equilibrium partition isotherms. Numbers in parentheses refer to systems listed in Table 2.

It may be argued that the solute molecules were preferentially adsorbed on the pore walls to an extent just sufficient to counterbalance the exclusion effect. However, it seems unlikely that the two phenomena would exactly offset each other for the many cases shown. Since preferential solute adsorption is expected to be temperature-dependent while the exclusion effect is presumably independent of temperature, the value of K_p for cycloheptaamylose in water was determined at a higher temperature (43°C). No significant change was observed.

In the diffusion studies, which are discussed below, the ratios of effective to bulk diffusivity for sugars in water agreed with values observed for other systems in which no preferential adsorption occurred (Figure 3), and these ratios were significantly higher than those observed for systems of similar molecular size but in which preferential adsorption definitely occurred. From all the evidence it seems likely that the sugars were not preferentially adsorbed and therefore that the exclusion effect was not significant. This suggests that the simple geometric argument used to derive Equations (3) and (4) is not applicable to the conditions investigated in this study.

The alkyl benzenes were all adsorbed to approximately the same extent ($K_p \sim 4$) at low concentrations. However, phenyl derivatives of benzene were more strongly adsorbed, the magnitude of this effect increasing with the number of aromatic rings in the molecule. K_p was about 12 for o-terphenyl, which contains three aromatic rings, and it was about 182 for triphenyl benzene, which contains four aromatic rings. This behavior is qualitatively consistent with the unusually strong intermolecular forces associated with molecules having high mobility, easily displacable π electrons (Margenau and Kestner, 1969). If it is assumed that the exclusion effect was also not significant for these molecules, then $K_p - 1$ represented the ratio of adsorbed solute to free solute within the pore. This was equivalent to only a small fraction of a monolayer coverage (always less than 10%) in the dilute concentrations employed in the diffusion studies, even for the most strongly adsorbed species.

Diffusion of Nonadsorbed Solutes

Results of all the diffusion studies are summarized in Table 2. Values of the bulk diffusivity in free solution were taken from the literature or estimated from related data using a modification of the approach proposed by Wilke (1949). Details are given by Pitcher (1972). Tabulated values of K_p correspond to the mean free concentration within the pores during the course of the runs.

Within groups of comparable K_p, the ratio of effective to bulk diffusivity decreased with an increase in the ratio of critical molecular diameter to pore diameter. The log of D_{eff}/D_0 was approximately inversely proportional to λ, as shown in Figure 2. The best straight line from least squares analysis which fits the data for nonadsorbing solutes is given by

$$\log_{10} (D_{eff}/D_0) = -0.37 - 2.0\lambda \qquad (8)$$

The extrapolated value of D_{eff}/D_0 for zero solute diameter 0.43 should correspond to the reciprocal of the tortuosity ($\tau = 2.3$). This compares favorably with the range $\tau = 2.1$ to 2.4 reported for porous silica-alumina having surface areas and pore volumes similar to the material used in this study (Weisz and Schwartz, 1962). This suggests that Equation (8) may be written more generally as

$$\log_{10} (D_{eff}\tau/D_0) = -2.0\lambda \qquad (9)$$

This simple empirical correlation may have usefulness in other applications with pore sizes commensurate with that investigated here. It is noteworthy that the exponential dependence of D_{eff}/D_0 on solute diameter has also been observed with other systems (Colton et al., 1971; Moore and Katzer, 1972).

The nonadsorbing solutes in Figure 2 represent various solute-solvent diameter ratios and gross overall conformations. The latter includes molecules which are roughly spheres, disks (for example, substituted benzenes and cyclodextrins), and cylinders (hexane, decane, and hexadecane with length: diameter ratios of 2.1, 3.1, and 4.7, respectively). These factors all appear to be of secondary importance.

The dashed curve in Figure 2 is the predicted result for K_r/τ as deduced from the exact solution of Haberman and Sayre (1958) for the increased drag on a sphere in creeping flow along the axis of a cylinder. The experimental

Table 2. Experimentally Measured Effective Diffusion Coefficients (25°C)

System number	Solute	Solvent	K_p*	λ	Diffusivity cm²/s × 10^5 D_0**	D_{eff}	D_{eff}/D_0
Nonadsorbing solutes							
1	sodium chloride	water	1.0	0.088	1.48^1	0.460	0.311
2	hexane	cyclohexane	1.0	0.153	1.80^2	0.330	0.183
3	*n*-decane	hexane	1.0	0.153	3.00^3	0.550	0.183
4	*n*-hexadecane	2,2,4-trimethyl pentane	1.0	0.153	1.50^3	0.260	0.173
5	*n*-hexadecane	hexane	1.0	0.153	2.21	0.440	0.209
6	cyclohexane	2,2,4-trimethyl pentane	1.0	0.203	2.64	0.490	0.185
7	2,2,4-trimethyl pentane	methyl cyclohexane	1.0	0.209	1.40	0.203	0.145
8	methyl cyclohexane	2,2,4-trimethyl pentane	1.0	0.209	2.40	0.390	0.163
9	glucose	water	1.0	0.269	0.673^4	0.101	0.150
10	sucrose	water	1.0	0.291	0.521^4	0.068	0.131
11	1,3,5-triisopropyl cyclohexane	2,2,4-trimethyl pentane	1.0	0.328	1.50	0.172	0.115
12	cyclohexaamylose	water	1.0	0.460	0.344^4	0.0148	0.0430
13	cycloheptaamylose	water	1.0	0.506	0.322^4	0.0124	0.0385
Preferentially adsorbed solutes							
14	1-octene	hexane	2.4	0.153	3.60	0.580	0.161
15	toluene	2,2,4-trimethyl pentane	3.5	0.197	3.20	0.284	0.089
16	cumene	2,2,4-trimethyl pentane	3.4	0.209	2.50	0.243	0.097
17	*m*-diisopropyl benzene	2,2,4-trimethyl pentane	4.0	0.231	1.90	0.104	0.055
18	1,3,5-trimethyl benzene	2,2,4-trimethyl pentane	4.0	0.262	2.50	0.179	0.072
19	1,3,5-triethyl benzene	2,2,4-trimethyl pentane	4.0	0.287	1.90	0.117	0.062
20	1,3,5-triisopropyl benzene	2,2,4-trimethyl pentane	4.1	0.300	1.60	0.094	0.059
21	o-terphenyl	2,2,4-trimethyl pentane	12	0.275	2.10	0.033	0.0157
22	1,3,5-triphenyl benzene	2,2,4-trimethyl pentane	182	0.381	1.40	0.0041	0.00029

* Average value for all runs, corresponding to time-mean concentration in pores.

** Where not otherwise indicated, values of D_0 were estimated (Pitcher, 1972) by a modification of the method of Wilke (1949).

[1] Harned and Hildreth (1951); Stokes (1950).

[2] Leffler and Cullinan (1970).

[3] Shieh and Lyons (1969).

[4] French (1957).

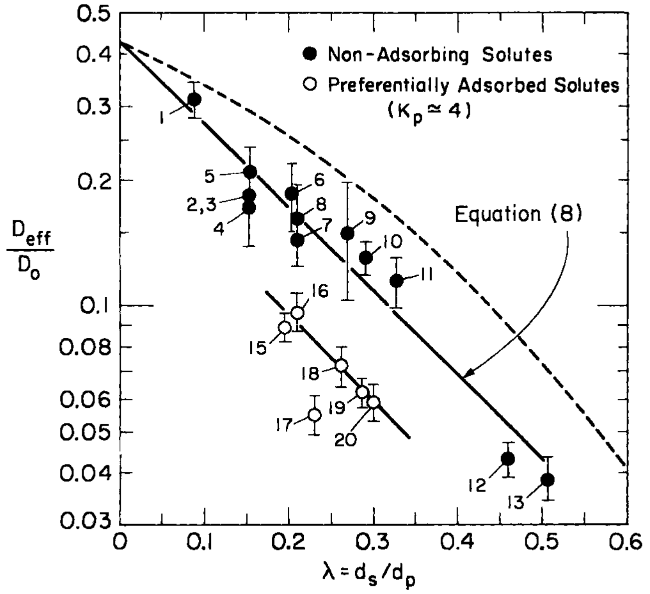

Fig. 2. Effect of ratio of solute critical diameter to pore diameter on effective diffusivity. Dashed curve is analytical solution for K_r/τ from Haberman and Sayre (1958). Numbers in parentheses refer to systems listed in Table 2. Error flags denote measured standard deviation.

data points clearly lie below the prediction of the hydrodynamic restricted diffusion model. The difference between the data and the theoretical prediction cannot be accounted for by off-axis position of the molecules, by the presence of noncylindrical pores, or by the asymmetry of the molecules. Bean (1972) has suggested that an area-mean integral of K_r obtained by integration across the cylinder radius should be employed to account for the locally increased drag experienced near the walls. The results of this calculation (Pitcher, 1972), using the first-order solution of Famularo as cited by Happel and Brenner (1965), show that the reduction in K_r is always less than 10% of its axial value. Bean's result (Curve C of his Figure 12) shows a greater effect and in fact agrees very closely with the data in Figure 2. However, the precise basis of Bean's calculation is not clear. The effect of noncylindrical pores (for example planar pores) is to increase K_r, and the correction for nonspherical particles of the asymmetry investigated here is small (Happel and Brenner, 1965). The experimental results therefore suggest that the hydrodynamic restricted diffusion model is not applicable to the 3.2 nm pores investigated in this study, perhaps because of a breakdown in the assumption of a continuum within the pore.

Figure 3 is a plot of $D_{eff}\tau/D_0$ versus λ on semi-logarithmic coordinates for the data for nonadsorbing solutes from this study and the data of Beck and Schultz (1972). Their data at higher λ for ribonuclease is not included because of evidence for essentially irreversible adsorption (Beck, 1969). If it can be assumed that K_p was unity in the other experiments of Beck and Schultz, then the agreement with the results of this study further supports the utility of Equation (9). The validity of the above assumption cannot at the moment be verified because equilibrium partition coefficients were not measured.

Diffusion of Preferentially Adsorbed Solutes

Figure 2 also presents results for the group of six substituted aromatics in 2, 2, 4-trimethyl pentane for which K_p was about 4. Values of D_{eff} were calculated in the same manner as that used when no preferential adsorption occurred. This is justified because all measurements were made in the concentration range where partition isotherms are linear. Preferential solute adsorption decreased D_{eff}/D_0 below the value at equivalent λ for the nonadsorbing solutes. Although the range of λ investigated with systems of $K_p \simeq 4$ is rather narrow, the roughly parallel behavior of the two sets of data implies that adsorbed solute molecules did not decrease the effective diameter of the pores. Had a narrowing of the pores occurred, a steeper slope would be expected on the coordinates of Figure 2 (where the same pore diameter is employed for both adsorbed and nonadsorbed solutes). The absence of significant pore narrowing is consistent with the relatively small amount of adsorption which, even under initial conditions, was equivalent to less than 5 to 10% of a monolayer.

If it is assumed that the free and adsorbed solute are in local equilibrium, that the latter is immobile, that the adsorption isotherm is linear, and that there is no exclusion of free solute, then the expression for D_{eff} which is compatible with Equation (6) is given by (Crank, 1957)

$$D_{eff} = D_f/K_p \qquad (10)$$

where D_f is the effective diffusion coefficient of free (that is, nonadsorbed) solute within the pores. It is assumed here that D_f is equal to D_{eff} for an equivalent-sized nonadsorbed solute and that it may be calculated from Equation (8). D_{eff} for the adsorbed solutes shown in Figure 2 ($K_p \sim 4$) is reduced by a factor of only about 1.7. A similar discrepancy exists for the more strongly adsorbed solutes (Table 2). For 0-terphenyl, K_p was about 12, but the reduction in D_{eff} was only by a factor of about 7.6 from

TABLE 3. CALCULATED SURFACE DIFFUSION COEFFICIENTS

System	D_s/D_0
In hexane:	
1-octene	0.125
In 2,2,4-trimethyl pentane:	
alkyl benzenes (average)	0.054
o-terphenyl	0.0069
1,3,5-triphenyl benzene	−0.00012

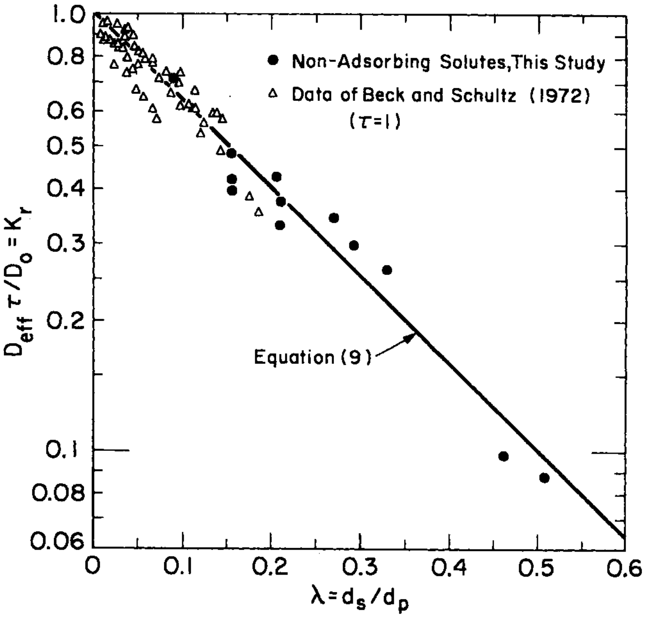

Fig. 3. Effect of ratio of solute critical diameter to pore diameter on effective diffusivity. Comparison with data of Beck and Schultz (1972).

an equivalent-sized nonadsorbed solute.

These observations imply that the adsorbed solute is mobile and contributes to the diffusion flux. Use of the classical surface diffusion model originally applied to gases (Barrer, 1965; Satterfield, 1970) leads to

$$D_{eff} = \frac{\frac{K_s S}{V_p} D_s + D_f}{\frac{K_s S}{V_p} + 1} \tag{11}$$

where D_s is the apparent surface diffusion coefficient of adsorbed solute and K_s is the slope of a linear adsorption isotherm which relates the surface concentration C_s (moles/area) to the free concentration C_f (moles/volume) by $C_s = K_s C_f$. Since $K_p = (K_s\, S/V_p) + 1$, Equation (11) may be written

$$D_{eff} = \frac{(K_p - 1)\, D_s + D_f}{K_p} \tag{12}$$

Apparent surface diffusion coefficients calculated from Equation (12) and normalized by bulk diffusion coefficients are given in Table 3. D_s decreases as K_p increases, that is, as the magnitude of the interaction between solute and pore wall increases. The surface diffusion model does not fit all the data, however, as D_s is negative for 1, 3, 5-triphenyl benzene, the largest and most strongly adsorbed of the hydrocarbons studied. An increase of more than 40% in D_{eff} would have been necessary to make D_s positive for this solute, an amount far greater than the estimated experimental error of 10%.

The intermolecular forces of attraction between solute and pore surface extend some distance beyond the adsorbed molecules. It is therefore reasonable to postulate that strongly interacting molecules in the vicinity of the wall, but not necessarily all adsorbed, have a decreased translational mobility as compared to molecules in the core of the pore and that the mobility decreases sharply as the surface is approached. A detailed examination of this hypothesis is perhaps not justified by the scope of this paper or by the limited data available. However, some insight may be gained from a simple model which provides a limiting approximation to the picture described above.

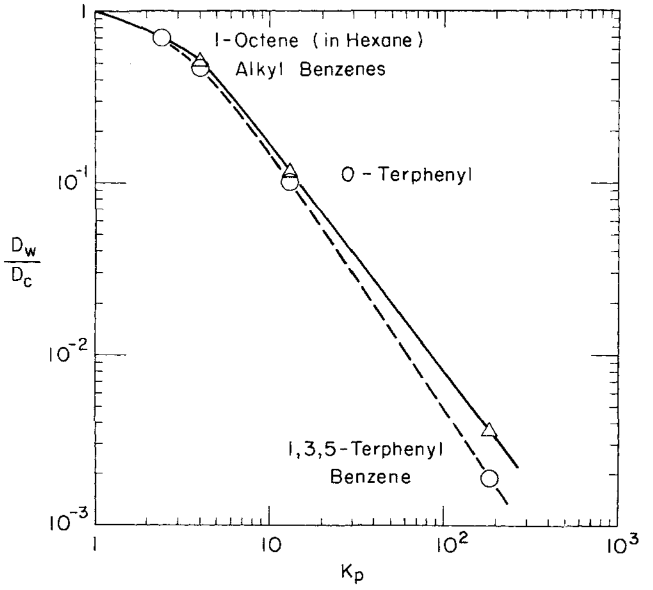

Fig. 4. Effect of magnitude of adsorption on diffusivity in wall region. Solvent is 2,2,4-trimethyl pentane except as indicated. ○ Thickness of wall region = solute critical diam. d_s. △ Thickness of wall region = thickness of molecule viewed as a disk (0.49, 0.47, 0.63, and 0.63 nm for 1-octene, alkyl benzenes, o-terphenyl, and 1,3,5-triphenyl benzene respectively).

Consider a cylindrical pore comprised of two distinct regions: a core in which solute-surface interactions are negligible and an annular wall region in which solute-surface interactions predominate. A cross-sectional area and solute diffusion coefficient are assigned to each region. The diffusivity characterizing the wall region is clearly an integrated average of molecules covering a range of mobilities. It is further assumed that the volumetric concentrations within these regions are at equilibrium at all times and are linearly related by $C_w = K_w C_c$. A detailed derivation is given elsewhere (Pitcher, 1972). The result is

$$D_{eff} = \frac{K_w \frac{A_w}{A_c} D_w + D_c}{K_w \frac{A_w}{A_c} + 1} \tag{13}$$

where

$$K_w = K_p\,(A_c/A_w + 1) - A_c/A_w \tag{14}$$

and subscripts c and w refer to core and wall regions, respectively. Equations (13) and (14) reduce to Equation (12) as $A_w \rightarrow 0$, and to $D_{eff} \rightarrow D_w$ as $A_c \rightarrow 0$.

The model contains an adjustable parameter A_w/A_c. A reasonable minimum value for A_w is the area circumscribing a layer one molecule thick. With this and the assumption that D_c equals D_{eff} for a nonadsorbing solute, values of D_w were calculated for the adsorbing systems, and the results are shown in Figure 4. D_w/D_c is positive for all solutes, less than unity, and relatively insensitive to moderate changes in the estimate of A_w/A_c. D_w decreases sharply with an increase in the magnitude of the interaction between solute and pore surface as measured by K_w. This trend is in qualitative agreement with the correlation developed by Sladek (1967) as discussed by Satterfield (1970) for surface diffusivities of gases and with the decreased effective diffusivity in zeolites with increasing solute adsorption as reported by Moore and Katzer (1972). However, quantitative use of this approximate model for predictive purposes must await further verification.

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NOTATION

a = sphere radius, cm
A_c = cross-sectional area of core region, cm^2
A_w = cross-sectional area of wall region, cm^2
C_b = solute concentration in bulk (external) solution, g/cm^3
C_c = solute concentration in core region, g/cm^3
C_f = concentration of free solute in pores, g/cm^3
C_p = total solute concentration in pores, g/cm^3
C_s = surface concentration of adsorbed solute, g/cm^2
C_w = concentration in wall region, g/cm^3
D_c = diffusivity in core region, cm^2/s
D_{eff} = effective diffusivity, cm^2/sec. Defined by Equation (6) for present study and by Equation (2) for steady state diffusion across a membrane

D_f = effective diffusivity of free solute, cm^2/s
D_0 = bulk diffusivity in free solution, cm^2/s
D_s = apparent surface diffusivity of adsorbed solute, cm^2/s
D_w = apparent diffusivity of solute in wall region, cm^2/s
d_p = pore diameter, nm
d_s = critical solute molecular diameter, nm
h = membrane thickness, cm
J = solute flux, g/cm^2-s
K_p = C_p/C_b, equilibrium partition coefficient
K_r = D_p/D_0, fractional reduction of diffusivity of nonadsorbed solute within pores resulting from proximity of the pore wall. K_r approaches unity as the ratio of molecular size to the pore size approaches zero
K_s = C_s/C_f, slope of linear surface adsorption isotherm, cm
K_w = C_w/C_c, wall region-core region equilibrium distribution coefficient; also defined by Equation (14)
S = specific surface area, cm^2/g porous solid
T = temperature, °K
t = time, s
V_p = specific pore volume, cm^3/g porous solid

Greek Letters

θ = pore volume fraction
λ = d_s/d_p, ratio of critical solute molecular diameter to pore diameter
μ = viscosity, g/cm-s
τ = tortuosity

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