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Liquid Diffusion in Microporous Alumina Pellets

The effect of the ratio of the molecular solute diameter to the pore diameter and adsorption equilibrium on the liquid phase effective diffusivity for different hydrocarbon solutes was studied in two alumina pellets. A semiempirical correlation based on the relative dimension of the solute molecule with respect to the average pore dimension, the equilibrium partition coefficient, and the porosity is proposed for a variety of binary hydrocarbon systems. The correlation shows that the effective diffusivity is strongly influenced by both the adsorption coefficient as well as the ratio of the solute molecular size to the average pore size.

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The rate of microsolute diffusion in liquids within microporous material such as solid catalysts has been seen to be less than would be observed in unrestricted liquid medium. This has been variously attributed to the existence of a hydrodynamic drag. Various models, theoretical as well as empirical, have related this drag coefficient to the ratio of the relative size of the diffusing molecular to the pore size.

While the effect of the ratio of the molecule size to the pore size has been the subject of a number of studies,

the simultaneous effect of this ratio together with the effect of adsorption equilibrium on diffusion in pores has been the subject of only a few studies. Though adsorption equilibrium has been shown to affect rates of diffusion in porous material (for example, Scatterfield, et al., 1973; Komiyama and Smith, 1974*a*), the exact relationship has not been the subject of definitive and exhaustive studies.

In this work, the diffusion of a number of solute hydrocarbons was studied in two different alumina pellets. The average pore diameters of the two samples are 56.9 and 66.4Å. The present study examined the effect of the molecule size and also the adsorption equilibrium on the diffusion rates of solutes in these microporous solids. The λ (ratio of solute molecule size to average pore size) values obtained in this study are less than 0.1. Effective diffusion coefficients were evaluated by transient diffusion measurements. The solute adsorption relationships were established independently from equilibrium measurements.

CONCLUSIONS AND SIGNIFICANCE

Effective diffusivity values in the pellets for the different solute-solvent systems were less than the unrestricted diffusivity values. The effective diffusivity values were found to depend on the ratio of the solute molecular radius to the average pore radius λ and also to the equilibrium partition coefficient K_p for a wide variety of solute-solvent system.

Effective diffusivity data for wide range hydrocarbon solute-solvent systems have been successfully correlated in terms of λ and K_p. Unlike the work of Satterfield et al., (1973), where the correlation was found to be on the basis of the solute critical radius, the work here suggests that the correlation is on the basis of the solute radius derived from molar volume values. The differences in the two correlations may be attributed to the range of λ obtained in the two studies. In the present study, λ values are generally less than 0.1, while those in Satterfield et al. (1973) are predominantly between 0.15 and 0.5. It is possible that at low λ it is the overall average molecule size which is the relevant dimension, while at higher λ values it is the critical diameter which is the important dimension.

The adsorption equilibrium isotherms obtained in this study suggest that whereas the exclusion effect may affect equilibrium partition coefficient values, the predominant effect seems to be that of the type of molecular species and surface effect.

BACKGROUND AND PREVIOUS STUDIES

Though a number of studies exist concerning diffusion in liquid filled pores of porous catalysts and other porous materials, understanding of diffusion of liquids in porous material is still limited because of the lack of success in isolating and understanding the different effects of simultaneous phenomena that exist during the diffusion of the species. An understanding of diffusion in porous material is important in predicting simultaneous diffusion and reaction rates and also in identifying different regimes of reaction. Moreover, if the effect of the different interacting phenomena can be mathematically modeled, then design of a new catalyst material in terms of pore sizes and distributions with respect to diffusing species would be immensely facilitated. This would especially be true with respect to petroleum residue and synthetic fuel, where macromolecules undergo reduction in their size both through thermal degradations as well as surface reaction in the pores of the catalyst.

The prevailing explanation for restricted diffusion in pores of small diameters ties the reduction of values of observed diffusivity in liquid filled pores as compared to unrestricted diffusivity values for different molecular species to the hydrodynamics. Because of the proximity of the molecule to the pore wall, it is postulated that there is an increase in frictional drag on the solute molecule with an increase in the ratio of the solute molecule diameter to the average pore diameter. Friedman and Kramer (1930) first suggested a quantitative estimate for the reduced diffusivity be employing the first-order solution of Ladenburg (1907) for the axial sedimentation of a hard sphere through a continuum bounded by a rigid cylinder. Faxen (1923) treated theoretically the problem of a rigid sphere in a cylindrical tube and gave an approximate series solution for the drag coefficient

$$K_d = 1 - 2.104\lambda + 2.09\lambda^3 - 0.95\lambda^5 \qquad (1)$$

where λ is the ratio of the sphere diameter to cylinder diameter. This coefficient combined with the partition coefficient K_p given by Ferry (1936) to account for the exclusion effect has been used by Lane (1950), Renkin (1954), and Ackers and Steere (1962) to give the value of the restricted diffusivity. Thus, according to them

$$D_{\mathrm{eff}} = D_o K_p K_d = (1 - \lambda)^2(1 - 2.104\lambda + 2.09\lambda^3 - 0.95\lambda^5) \qquad (2)$$

Haberman and Sayre (1958) obtained an exact solution to the fluid dynamic problem valid up to $\lambda = 0.8$, and this has been reviewed by Happel and Brenner (1965). Uzelac and Cussler (1970) used the equation

$$D_{\mathrm{eff}} = \frac{kT}{6\pi\eta a K_d} \qquad (3)$$

and found substantial agreement for experimental data involving the diffusion of polystyrene latex through Millipore filters. The drag coefficients K_d used are those from the exact solution of a sphere in a cylinder as tabulated in Happel and Brenner (1965).

Equation (1) and (2) has been applied to solute diffusion through biological membranes and swollen hydrophilic membranes (for example, Stein, 1967; Lakshminarayanaiah, 1969; Renkin, 1954; Ackers and Steere, 1962). Colton et al. (1971) and Satterfield et al. (1973) reported results on the diffusion of macrosolutes through porous media and obtained empirical relationships in terms of the ratio of the solute critical radius and the pore radius. The exact form of the relationship has been given by Satterfield and co-workers (1973) as

$$\log_{10} \frac{D_{\mathrm{eff}r}}{D_o} = -2.0\lambda \tag{4}$$

However, Colton et al. (1975) found the picture more complicated for studies involving the diffusion of macromolecules. Equation (4) was found to be less successful in correlating diffusivity data for macromolecules.

It is possible that some factors affecting the interpretation of diffusion data have not been dealt with extensively. Though attempts have been made to incorporate the exclusion effect as in Equation (2), very few studies exist where surface interaction effects have been dealt with in the basic diffusion equation models to account for its effect in the case of diffusion in liquid filled pores.

Pitcher (1972) and Satterfield et al. (1973) successfully correlated diffusivity data with respect to micromolecules having partition coefficients $K_p = 1$ but found that the effective diffusivity data involving systems having K_p values very much above 1 are several times smaller than the values predicted by the correlation given in Equation (4).

If local equilibrium can be assumed to exist in the pores, and there is a significant preference for the solute or the solvent, then it can be mathematically proven that the concentration gradient for the solute in the pores would be different for different values of the partition coefficient, though the bulk diffusivity and the concentration of the solute external to the beads are the same in each case. If dynamic equilibrium can be assumed, then the effect of the adsorption on the material balance equation could be modeled like a chemical reaction. Crank (1975) has discussed this situation where the effect of adsorption has been shown to be analogous to the effect of instantaneous reaction, which really slows down the diffusion process.

Looking at this in another way, Komiyama and Smith (1974*a*, *b*) postulated a parallel diffusion model where both bulk pore diffusion as well as surface diffusion takes place in the pore. Models of this sort have been relatively widely used for diffusion of gases in porous medium. It is easy to conceive and justify a parallel diffusion model in gases by hypothesizing that the solute molecule hops from one adsorption site to another. In this way surface diffusivity can be related to the effective bond energy between adsorbate molecules and adsorbent surface (for example, Higashi et al., 1963) or through some analogous mechanistic hypothesis (for example, Gilliland et al., 1974). For liquid systems, such a hypothesis does not appear appropriate since, unlike vapor or gaseous systems, the adsorbed molecule is closely surrounded by solvent or other adsorbate molecules. A model based on dynamic equilibrium between adsorbent surface and liquid in the pore, where a statistical number of solute molecules are always immobile at any time (or not available for bulk diffusion), seems to be more appropriate.

In the present work, effective diffusivity data in two different alumina pellets for a variety of solute-solvent systems are examined in terms of λ and the equilibrium adsorption isotherm. The solutes are chosen such that λ is less than 0.1 so that the assumptions on a continuum are at least approximately satisfied.

MATHEMATICAL MODEL FOR DIFFUSION WITH ADSORPTION

In treating the dynamic adsorption data, the following assumptions are made.

1. The physical adsorption or desorption step in the pores is rapid compared to the intraparticle diffusion.
2. The solute and the solvent concentrations in the pores and on solid are in equilibrium.
3. The adsorption isotherm is linear.

If we assume linear adsorption, the surface concentration may be written as

$$q = K_s C \tag{5}$$

The conservation equation in cylindrical coordinates in the particles can be written as

$$\epsilon \frac{\partial C_r}{\partial t} + \frac{\partial q}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r}\left(r D \epsilon \frac{\partial C_r}{\partial r} \right) \tag{6}$$

Substituting Equation (5) in (6) and expressing the surface adsorption coefficient K_s in terms of ϵ and the partition coefficient K_p, we obtain

$$\epsilon \frac{\partial C_r}{\partial t} + \frac{\partial}{\partial t}\left[\epsilon (K_p - 1) C_r\right] = \frac{1}{r} \frac{\partial}{\partial r}\left(r D \epsilon \frac{\partial C_r}{\partial r} \right) \tag{7}$$

which simplifies to

$$\frac{\partial C_r}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r}\left(r \frac{D}{K_p} \frac{\partial C_r}{\partial r} \right) \tag{8}$$

It is interesting to note at this point the effect of incorporating an adsorption term into the conservation equation. The effect of incorporating this term (assuming linear adsorption) is to reduce the diffusivity by a factor K_p as can be seen in Equation (8). It implies that for strong adsorption of solute ($K_p > 1$), the diffusion rate would be reduced, whereas for the strong adsorption of solvent ($K_p < 1$), the diffusion rate for solute would be increased.

For adsorption or desorption experiments with infinite fluid surrounding the pellets (that is, $\alpha = V/v \to \infty$), the initial and boundary conditions are

$$t = 0 \quad C = C_1 \quad o < r < a \tag{9}$$

$$t > 0 \quad C = C_o \quad r = a \tag{10}$$

$$\left(\frac{\partial C}{\partial r} \right)_{r=0} = 0 \tag{11}$$

If M_t denotes the quantity of diffusing solute which has entered or left the pellet in time t and M_∞, the corresponding quantity after infinite time, then the solution of Equation (8) with (9) to (11) for an infinite cylinder in terms of the fractional uptake is (Crank, 1975)

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{4}{a^2 \alpha_n^2} \exp\left(- \frac{D \alpha_n^2 t}{K_p} \right) \tag{12}$$

where α_n's are the roots of the Bessel function of the first kind of order zero

$$J_0(a\alpha_n) = 0 \tag{13}$$

For small times, the solution for the calculation of the fractional uptake is more easily handled if the following expression is used (Crank, 1975):

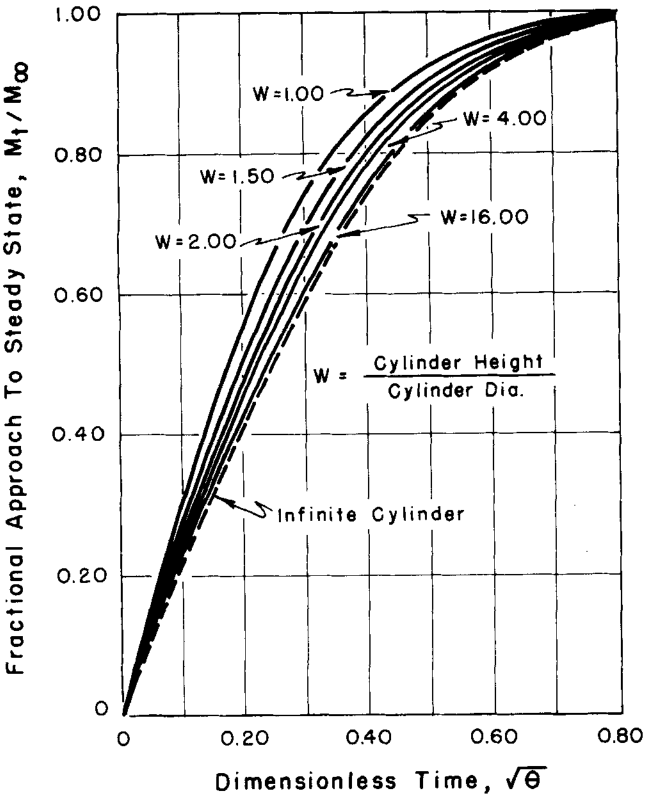

Fig. 1. Approach to steady state vs. dimensionless time for a cylinder for $\alpha \to \infty$.

$$\frac{M_t}{M_\infty}=\frac{4}{\pi^2}\left(\frac{Dt}{K_pa^2}\right)^{1/2}-\left(\frac{Dt}{K_pa^2}\right)-\frac{1}{3\pi^{1/2}}\left(\frac{Dt}{K_pa^2}\right)^{3/2}+\ldots \quad (14)$$

For the case of a finite cylinder in an infinite medium, the solutions to the two-dimensional diffusion equation has been numerically computed by Ma and Evans (1968) using the Neuman product technique. Both the solutions to the infinite cylinder and the finite cylinder for different ω (ω = length of cylinder/diameter of cylinder) are shown in Figure 1, which is a plot of M_t/M vs. $\theta^{1/2}$, where $\theta = Dt/K_pa^2$.

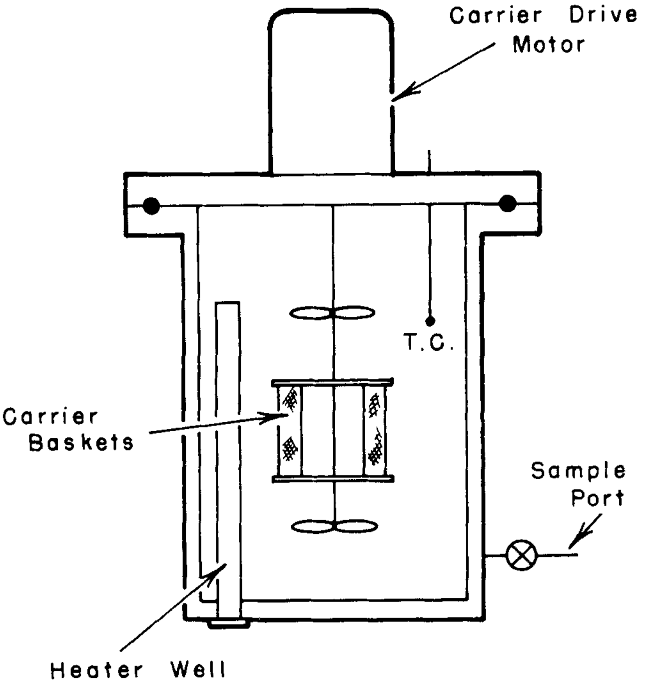

Fig. 2. Well-stirred reactor used for diffusion experiments.

As can be seen from Figure 1 at low values of ω, the solution to the differential equation is significantly influenced by ω. At $\omega > 16$, for example, the solution approaches the solution for the infinite cylinder.

The diffusivity term D in Equation (8) incorporates τ in the case of diffusion of solute through a porous structure. If the diffusivity is also postulated to depend on the solute radius and the pore radius, then the effective diffusivity D_{eff} may be written in terms of the unrestricted diffusivity D_o according to the model referred to previously as

$$D_{\text{eff}} = \frac{D_o}{K_p\tau} f(r_s, r_p) \quad (15)$$

where $f(r_s, r_p)$ is some function of the solute radius and pore radius.

EXPERIMENT

Materials

The porous materials used in this study were alumina pellets. The mean pore radius based on volume for WP-1 is 66.4 Å, while that for WP-2 is 56.9 Å. The pellets as received are cylindrical in shape with a diameter of about 0.32 cm. For each experiment, the pellets were chosen in such a way that ω for each pellet varied only by ± 5% from the average value.

Solute-solvent systems covering a wide range of molecular volumes were chosen as shown in Table 1. Reagent grade chemicals were used whenever possible, and in cases where not possible the chemicals used were invariably in excess of 99% purity. The molecular radii used in this study corresponded to the radii of the molecules computed from molar volumes of compounds at their boiling point.

Apparatus and Procedure

The experimental work fell into two divisions: transient diffusion experiments and equilibrium adsorption measurements. In

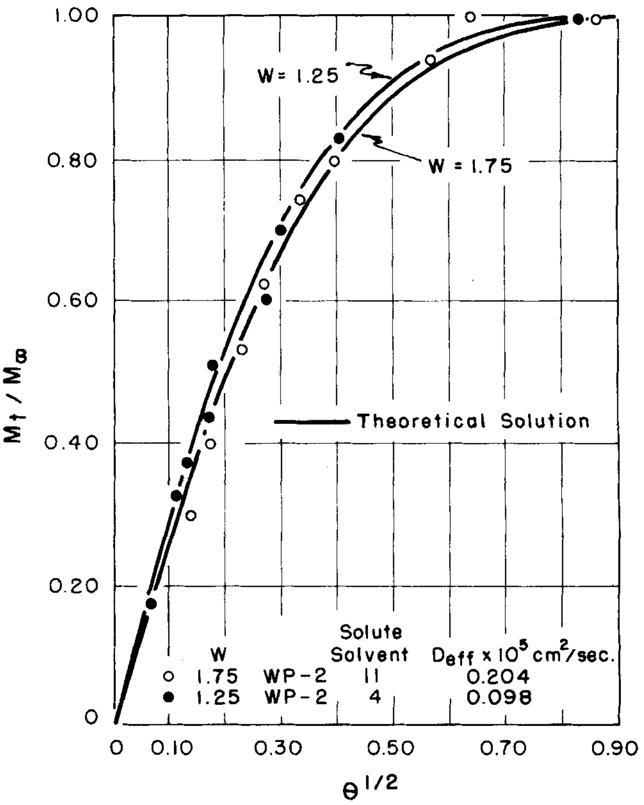

Fig. 3. Plot of diffusion data compared to theoretical curves.

TABLE 1. EXPERIMENTAL VALUES OF EFFECTIVE DIFFUSION COEFFICIENTS AND EQUILIBRIUM PARTITION COEFFICIENTS

WP-1 pellets

No.	Solute	Solvent	T	K_p	$\lambda \times 10^2$	Diffusivity cm²/s × 10^5 D_o†	D_{eff}	$\frac{D_{eff} K_{p\tau}}{D_o}$
1	1-methylnaphthalene	Benzene	25°C	1.03	6.13	1.48	0.963	1.06
2	Tetralin	Benzene	25°C	1.21	6.04	1.52	0.960	1.21
3	Cis-decahydronaphthalene	Benzene	24°C	1.20	6.30	1.39	0.665	0.911
4	Trans-decahydronaphthalene	Benzene	24°C	1.20	6.30	1.39	0.725	0.993
5	Ethylbenzene	Benzene	25°C	1.00	5.75	1.66	1.08	1.03
6	Styrene	Benzene	25°C	1.48	5.65	1.72	1.03	1.41
7	*p*-xylene	Hexane	26°C	1.25	5.75	3.26	1.62	0.986
8	*p*-xylene	Benzene	25°C	1.23	5.75	1.66	1.32	1.55
9	Mesitylene	Benzene	25°C	1.18	6.04	1.52	0.922	1.14
10	Cyclohexane	Toluene	24.5°C	0.941	5.43	2.17	2.06	1.42
11	Methylcyclohexane	Toluene	25°C	1.21	5.75	1.97	1.52	1.48
12	2,2,4-trimethylpentane	Toluene	25°C	1.02	6.30	1.67	0.787	0.763
13	Biphenyl	Benzene	24.3°C	1.10	6.30	1.39	0.566	0.711
14	1-hexene	Benzene	24.5°C	1.04	5.65	1.70	1.37	1.33
15	1-octene	Toluene	24°C	1.05	6.22	1.68	0.740	0.734
16	1-nonene	Toluene	24.3°C	1.07	6.47	1.58	0.921	0.990
17	1-decene	Benzene	24.3°C	0.854	6.70	1.25	1.05	1.14
18	Hexane	Benzene	25°C	0.886	5.75	1.66	1.55	1.31
19	Heptane	Toluene	25°C	0.982	6.04	1.80	1.46	1.26
20	Octane	Benzene	25°C	0.900	6.30	1.41	1.33	1.35
21	*o*-terphenyl	Toluene	25°C	0.940	7.18	1.32	0.394	0.445
22	1,3,5-triethylbenzene	Cyclohexane	25°C	1.20	6.77	0.884	0.333	0.717
23*	*m*-xylene	Benzene	25°C	1.24	5.75	1.66	0.705	0.836
24*	*o*-xylene	Benzene	24.5°C	1.22	5.75	1.65	0.610	0.716

WP-2 pellets

No.	Solute	Solvent	T	K_p	$\lambda \times 10^2$	Diffusivity cm²/s × 10^5 D_o†	D_{eff}	$\frac{D_{eff} K_{p\tau}}{D_o}$
1	1-decene	Cyclohexane	25°C	1.00	7.82	0.901	0.303	0.530
2	*n*-nonane	Cyclohexane	25°C	0.779	7.64	0.939	0.334	0.436
3	*m*-xylene	Benzene	25°C	1.27	6.71	1.66	0.562	0.677
4	1,3,5-triisopropylbenzene	Cyclohexane	25°C	1.19	8.60	0.758	0.098	0.242
5	2,2,4-trimethylpentane	Toluene	24.5°C	0.914	7.35	1.66	0.714	0.619
6	*n*-heptane	Toluene	25°C	0.901	7.05	1.80	1.05	0.828
7	1,3,5-triethylbenzene	Cyclohexane	25°C	1.06	7.90	0.884	0 272	0.514
8	Tetralin	Benzene	25°C	1.22	7.04	1.52	0.614	0.776
9	1-hexene	Methylcyclohexane	25°C	1.04	6.59	1.71	0.779	0.746
10	Mesitylene	Toluene	25°C	1.23	7.05	1.80	0.716	0.770
11	1-methylnaphthalene	Cyclohexane	25°C	2.03	7.15	1.06	0.204	0.615
12	Cumene	Cyclohexane	25°C	1.17	7.05	1.09	0.481	0.813
13*	Ethylbenzene	Benzene	25°C	0.997	6.71	1.66	0.333	0.315

* For the diffusion runs only, the pellets were not activated first to remove moisture.
† Values estimated using Wilke-Chang equation.

the case of the diffusion experiments, the solute concentrations were measured using a GowMac Flame Ionization Chromatograph. The concentrations for solute involved in the experiments on diffusion from the pellets into the solvent medium ranged from a few hundred parts per million to less than 0.1%. Because of this, extreme precautions had to be taken in column, temperature, and flow rate selection so as to obtain the widest possible separation between solute and solvent peaks.

For the diffusion runs, the agitated reactor shown in Figure 2 is used. The agitator consists of a shaft driven by a variable speed motor. The shaft carries an agitator as well as two carrier baskets made out of 40 mesh wire. The carrier baskets can be emplaced within 3 or 4 s on the shaft. The reactor has eight baffles and is 1.5 l in volume. The pellets are first activated to remove moisture from them by heating them for an hour at 200°C. They are then placed in the carrier baskets and left to equilibrate with a solute-solvent solution generally of 10 to 15% strength for a day or two. Before the diffusion run, the pellets together with baskets are rinsed with pure solvent to remove solution clinging to outside of pellets and baskets and then are immediately placed on the impeller shaft, the reactor with the solvent in it is raised, and the agitator started. The whole operation between rinsing and the start of the run takes less than 10 to 12 s.

The amount of pellets used is usually between 3 to 5 g and the amount of solvent in the agitated vessel between 650 to 8C0 cm³. Thus, the ratio α is always between 150 to 250, which ensures approximately constant boundary conditions for the diffusion run.

The temperature is controllable to within ± 0.5°C throughout the diffusion run. Most of the experiments take between 1 and 2 hr, though 90% fractional uptake is usually accomplished in most cases within 45 min. The solvent in the reactor is usually sampled at least between six and ten times before 90% fractional uptake is accomplished. Each sampling is preceded by draining of the needle valve attached to the reactor to the extent of six or seven drops, which is the estimated volume in the line. Then about 1 cm³ is collected as a sample for the analysis. The whole operation of draining and sampling takes less than 5 s each time.

Figure 3 shows the diffusion data generated for a few solute-solvent systems.

The impeller and basket speeds used are generally around 600 rev/min. This speed is substantially above the speed such

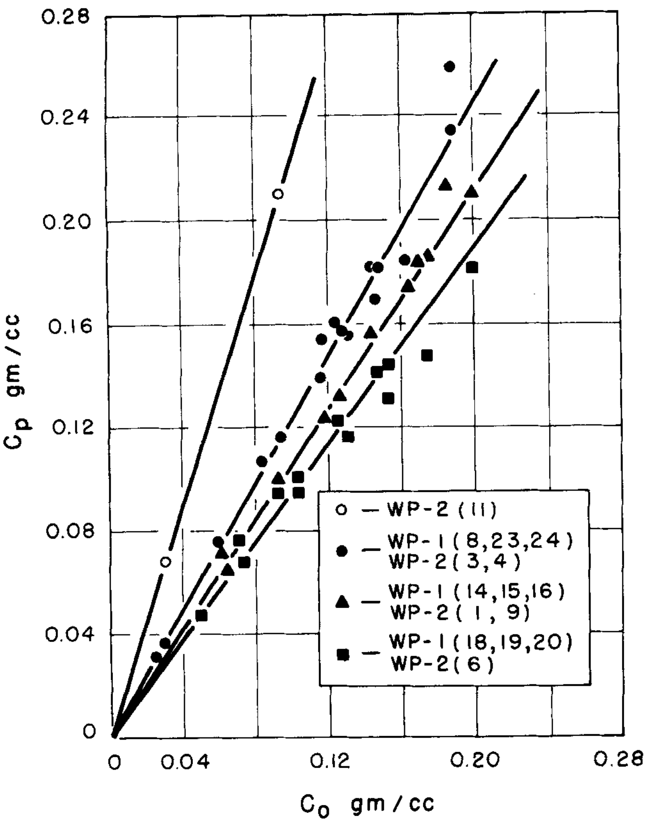

Fig. 4. Adsorption isotherms for different solute-solvent systems for WP-1 and WP-2 pellets.

that external mass transfer effects could affect diffusivity results. This was verified through experimental runs by varying speeds as well as calculation using estimated mass transfer coefficients. The reactor temperature was measured by a thermocouple.

Fractional approach to equilibrium at time t is defined in terms of concentration in the reactor as $(C_t - C_i)/(C_\infty - C_i)$, where subscripts i and ∞ refer to conditions at the start of the experiment and after the system has come to an equilibrium. C_i was assumed to be 0 in all the experiments. Independent tests conducted by immersing the baskets in a solvent in a beaker after the first rinse for a second or two confirmed that the concentration is indeed essentially 0.

C_t and C_∞ were always corrected for solution withdrawn from the reactor for prior samples prior to the sampling at time t. The total amount of solvent withdrawn for all the samples and rinses is usually less than 2%, so that the correction for C_t ranged from a fraction of a percent in the first sample to something less than 2% for C_∞. Then, with these values of M_t/M_∞, D_{eff} was calculated from the solution to the diffusion equations in two dimensions represented by the plots of M_t/M_∞ vs. $D_{\text{eff}}\ t/a^2$ for a cylinder as shown in Figure 1. D_{eff} was measured from at least five or six values of M_t/M_∞ vs. t. The average values are obtained by averaging at least five values. Care is always taken to use M_t/M_∞ values well below 0.9 for averaging D_{eff} because there is greater scope for error beyond this value since the solution for M_t/M_∞ approaches the asymptotic values of 1.0 rather slowly.

For the equilibrium adsorption studies, about 1 to 2 g of pellets are contacted with about 3.5 g of solution of known concentration in air tight bottles to prevent vaporization of solution. The bottles are immersed in a constant temperature bath for a day or two with occasional shaking to hasten equilibrium. After the solution has reached equilibrium, the solution surrounding the pellets is analyzed. From the initial and final concentrations and the pore volume of the catalyst, the average concentration in the pellets can be obtained by a mass balance. For each solute-solvent-pellet system, equilibrium partition coefficient is in most of the cases established for two or three concentrations. The equilibrium adsorption studies were conducted at the temperature of the diffusion runs. The temperature variation during each experiment was much better than ±1°C.

RESULTS AND DISCUSSION

Equilibrium Studies

Typical results of the equilibrium partition experiments are shown in Figure 4, where solute concentration inside the pores is plotted vs. solute concentration in the external liquid surrounding the pellets. The following groups of solute-solvent systems were studied both for equilibrium partition experiments as well as diffusion experiments: (1) substituted aromatics as solutes and either benzene or toluene or cyclohexane as solvent, (2) naphthalene ring compounds as solutes and single ring aromatics as well as cyclohexane as solvents, (3) straight chain paraffinic compounds, 2,2,4-trimethylpentane, and cycloparaffins as solutes with the same solvents as in number 2, (4) straight chain olefins as solutes and the solvents listed in number 2. In the range of concentrations used for the diffusion experiments, the isotherms were found to be linear.

The values of K_p obtained range approximately from 0.8 to 2.0. Most of the values, however, range from 0.8 to 1.30. There are some definite trends that can be observed. For example, in the case of WP-1 pellets, the equilibrium partition coefficient for the straight chain paraffins is close to 0.9 for aromatic solvents, while that of the 1-olefins are generally somewhat above 1.0. If we assume that the surface of the pellet is active, it is logical to obtain K_p values which are lower for the paraffins as compared to the olefins, 2,2,4-trimethylpentane has larger K_p values than the paraffins, presumably because the methyl groups on the pentane molecule induce a shift in the electrons to make the molecule somewhat more polar.

The partition coefficient values obtained here do not seem to substantiate the concept put forth by Ferry (1936) in terms of a geometric exclusion effect. Ferry gave the following equation for the partition coefficient:

$$K_p = (1 - \lambda)^2 \tag{16}$$

By similar reasoning, Satterfield et al. (1973) suggested

$$K_p = \frac{[1 - \lambda \text{ solute}]^2}{[1 - \lambda \text{ solvent}]^2} \tag{17}$$

when the size of the solvent molecule is also significant with respect to the pore diameter.

When we look at the partition coefficient values for the aromatic-aromatic systems, it is clear that the substituted aromatics yielded values generally around 1.2 and above when used with benzene as a solvent. The substituted benzenes have average molecule radii larger than benzene. If the exclusion effect is significant, then K_p should be less than 1 in these cases as predicted by Equations (16) and (17).

The values $K_p = 1.2$ do not seem to be unreasonable, since the methyl, ethyl and other substituted groups on the benzene ring are supposed to remove the electronic symmetry of the benzene ring. If K_p is expressed on the basis of a surface adsorption coefficient as in Equation (5), then an approximate calculation in terms of an average molecule's cross-sectional area, porosity, surface area of pellet, and an assumption of at least a monolayer adsorption indicates that for $K_p = 1.2$ the concentration of solute molecules on the surface is anywhere from 70 to 150% more on the surface of the pellet than in the liquid surrounding the surface in the pores.

Generally, in the case of substituted aromatic solutes and cycloparaffin solvent, the K_p values obtained are greater than 1. In the case of WP-2 pellets and 1-methylnaphthalene-cyclohexane, $K_p \simeq 2$, while in the case of WP-1-1,3,5 triethyl benzene-cyclohexane system, $K_p \simeq 1.20$. Yet, in some cases the exclusion effect seems to affect the results slightly. In the case of the adsorption of o-terphenyl with toluene as a solvent, for example, K_p is close to or less than 1.

The average pore radius is large (66.4 and 56.9 Å for WP-1 and WP-2, respectively, on a volume basis), but a significant portion of the surface area of the pellet constitutes the surface area for pore sizes below 30 Å. The exclusion effect may be significant for this fraction of the pellet area in case of the bigger molecules like o-terphenyl. Or, stating it in another way, the value of K_p for similar chemical species may vary according to relative molecule sizes and pore sizes, and that the K_p which is observed is just an average value for the pore size distribution.

The results show that K_p is predominantly dependent on the nature of chemical species (for example, aromatic, substituted aromatic, double bonds, paraffin, etc.), but there may be smaller effects due to relative sizes of molecule and pore radii, though results for this are not conclusive.

Diffusion of Different Molecular Species

In the diffusion studies with the two types of pellets, a large number of studies were conducted with WP-1. But the same representative species were studied with WP-2. The pore distribution of the two catalysts are somewhat different. The average pore size for WP-1 is 66.4 Å, while that for WP-2 is 56.9 Å.

The effective diffusivity values for similar solute-solvent systems (for example, tetralin-benzene) are different from each other. The diffusivity value for tetralin in WP-1 is about 50% higher than in WP-2. When we consider the fact that the porosities of the two types of pellets are the same (and hence tortuosities are probably the same), the finding is consistent with the hypothesis that the pore size influences the diffusivity values. If the effective diffusivity, ordinary bulk diffusivity, and K_p are arranged in a manner consistent to the model proposed, the data plot very satisfactorily if the correlation is made vs. the molecular volume at the boiling point of the solutes, as can be seen from Figure 5 for the case of WP-2 pellets.

The effect of the partition coefficient K_p is significant. If this effect is neglected and data are plotted according to the various models investigated, the results do not show any statistical trends that are valid or significant. The data of Satterfield et al. (1973) and Pitcher (1972) substantiate this finding.

The hydrodynamic restricted diffusion models used by Haberman and Sayre (1958) and others represented by Equations (1), (2), and (3) were tried and failed to yield any valid correlation. We tried to correlate data using the empirical correlation provided by Satterfield et al. (1973) and found that the solute critical diameter (that is, the smallest geometrical dimension of the molecule) did not present a relevant basis to correlate our data. There could be a number of reasons for this, which will be discussed later.

Since the semilog plot of $D_{\text{eff}}K_p/D_o$ vs. the solute molecular volume at the boiling point yielded satisfactory correlations for each one of the pellets, the molecule radius for each one of the pellets (obtained from the molecular volume at the boiling point, predicted by the LeBas group contribution method) was made dimensionless by dividing it with the average pore radius. A tortuosity was estimated using the random pore model (Wakao and Smith, 1962). If the assumption behind the model presented here seems reasonable, Equation (15) can be rearranged in the following manner:

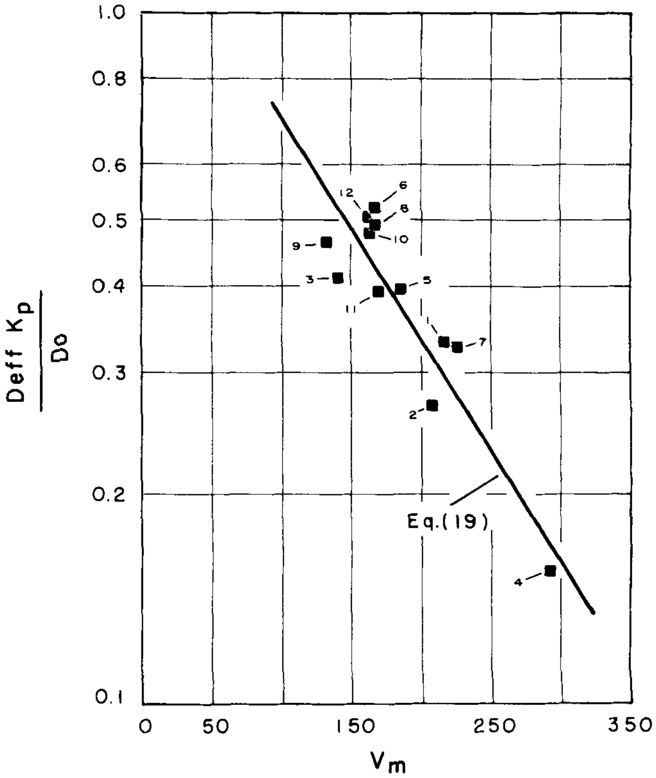

Fig. 5. Plot of $D_{\text{eff}}K_p/D_o$ vs. V_m for WP-2 pellets.

$$\frac{D_{\text{eff}}K_p\tau}{D_o} = f(r_s/r_p) \tag{18}$$

On this basis, the following empirical correlation is obtained:

$$\ln \frac{D_{\text{eff}}K_p\tau}{D_o} = a\lambda^3 + b \tag{19}$$

The 95% confidence limit values of a and b obtained from a linear regression are given below:

$$a = -3479.2 \pm 616.5$$

$$b = 0.863 \pm 0.19$$

The analysis of variance gives a standard deviation of 0.186. Figure 6 shows a semilog plot of $D_{\text{eff}}K_p\tau/D_o$. As can be seen from the figure, the data plot quite well for this correlation. The average deviation for the points around this correlation is less than 15%. This is a very satisfactory correlation for diffusion data, considering the fact that the number of data points is large and it involves two types of pellets of different pore size distributions.

The above correlation is the best correlation that we obtained using the data given in Table 1. In all fairness, we would like to report that we obtained a satisfactory, though statistically less attractive, model based on a linear correlation with respect to λ of the form (Figure 7)

$$\ln \frac{D_{\text{eff}}K_p\tau}{D_o} = a\lambda + b \tag{20}$$

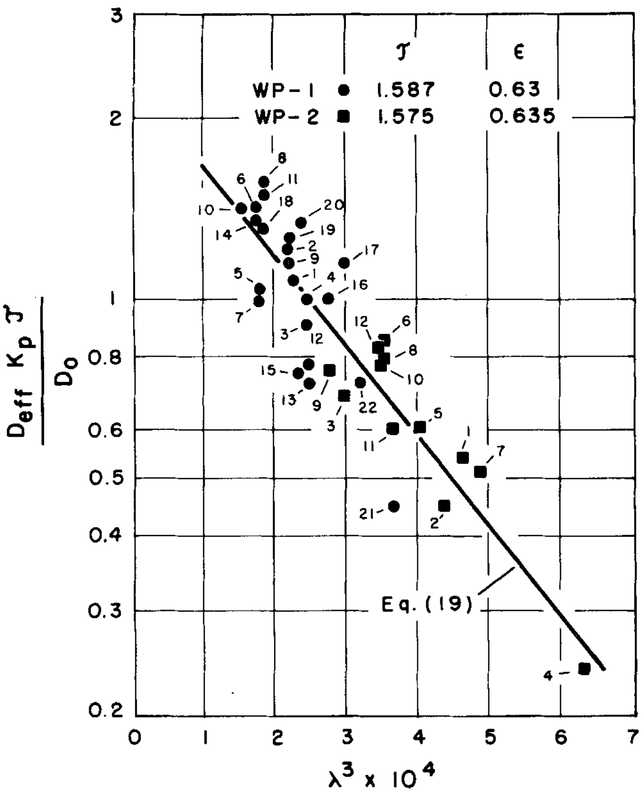

Fig. 6. Correlation of effective diffusivities on the basis of λ^3.

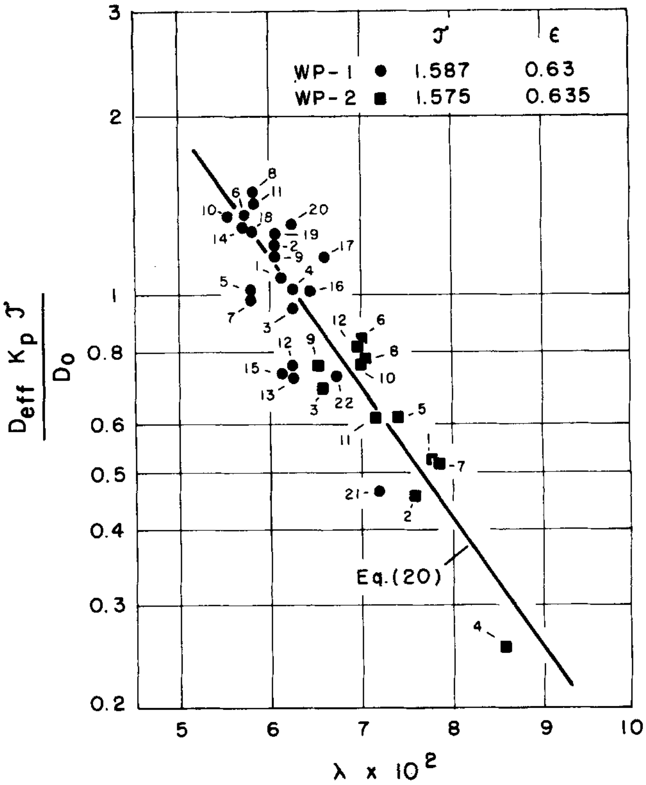

Fig. 7. Correlation of effective diffusivities on the basis of λ.

When analyzed on the basis of this correlation, the constants a and b have values within the following 95% confidence limits:

$$a = -49.3 \pm 8.8$$

$$b = 3.08 \pm 0.58$$

The analysis of variance yielded a standard deviation of 0.190. However, with this correlation used, the experimental data yielded a significantly greater scatter around the correlation. Moreover, the intercept value (that is, $D_{eff}K_p\tau/D_o$ as $\lambda \rightarrow 0$) appears more reasonable in case of the first correlation. Values of τ between 1 and 5 are often obtained. Though in the pellets used in this study, τ has not been experimentally determined, values 1.59 and 1.575, as predicted by the random pore model, have been used for WP-1 and WP-2, respectively. It has been suggested that the concept of τ is more complicated (Van Brakel and Heertjes, 1974) than the analysis based on the random pore model, and the actual values of τ for the samples may very well be different.

The correlations developed here are based on the average solute radius ($r_s = (3V_m/4\pi N)^{1/3}$). The molar volume V_m is calculated using the LeBas group contribution method (Reid and Sherwood, 1966). The analysis was first attempted by using the critical solute diameter as in the work of Pitcher (1972). This approach did not yield any statistically significant correlations. The results obtained for the linear correlation represented by Equation (21) are substantially different than the correlation put forward by Satterfield et al. (1973) for data of Pitcher (1972) and Beck and Schultz (1972) for which the equilibrium relationships are unknown and τ was assumed to be equal to 1 (Satterfield et al., 1973).

There are a number of possible reasons why the data obtained here and those reported by Satterfield et al. (1973) are different. The molecular sizes obtained in this study are a lot smaller than the pore size. For this reason, the overall average dimension of the molecule is most likely to be the relevant dimension for correlation of D_{eff}. In the case of molecules of comparable dimension as the width of the pores (as in Satterfield et al. where λ values are predominantly between 0.15 and 0.5), the critical molecular diameter may be the relevant dimension. Also, the pellets used in this study have a different pore distribution from those of the silica-alumina used in the study mentioned earlier.

It can thus be argued that where λ is large (that is, perhaps $\lambda > 0.15$ to $\lambda < 1$), the relevant dimension on which D_{eff} depends is the critical solute radius, whereas when λ is close to 0, relevant dimension may very well be the average radius as used in this study.

In all the discussion concerning diffusion in microporous material, it should also be borne in mind that at $\lambda >> 0$, concept of a continuum within the pore may not be valid, and the use of differential equations in treating diffusion in small pores (that is, for high values of λ) may not be even approximately correct. Satterfield and Cheng (1972), Satterfield and Katzer (1971), Moore and Katzer (1972), and Satterfield and Chiu (1974) reported diffusivity values for organic solutes in zeolites several orders of magnitude lower than bulk diffusivity values and seem to be also influenced by specific interactions between the solutes and the pore walls.

CONCLUSIONS

On the basis of this work, a number of conclusions may be drawn.

1. Models treating diffusion in liquid filled pores should take into account equilibrium relationships between diffusing solute and pore surface. Though partition coefficients obtained in this study varied by a factor less than 2 in most cases, the concentrations present on the surface, assuming monolayer adsorption, would be a few times that of the concentration in the pore as pointed

out earlier. The results obtained in this study together with previous work done by other workers strongly indicate that effective diffusivity of solutes in adsorbing porous material is influenced by the adsorption equilibrium.

2. The effective diffusivity varies according to an exponential cubic relationship in λ for small λ values.

3. There are probably different regimes for diffusion depending on the value of λ. The correlation for D_{eff} at high λ ($\lambda = 0.3$ to 0.5, for example) may be different from the correlation for D_{eff} at low λ.

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NOTATION

a = constant in Equation (19) or (20), also radius of cylindrical pellet
b = constant in Equations (19) or (20)
C = solute concentration in g/cm^3
C_i = solute concentration initially, g/cm^3
C_o = bulk solute concentration at equilibrium, g/cm^3
C_p = solute concentration in pores, g/cm^3
C_r = solute concentration at a radius r in pellet, g/cm^3
C_t = solute concentration at time t, g/cm^3
C_∞ = solute concentration at infinite time, g/cm^3
D = diffusivity of solute, cm^2/s
D_{eff} = effective diffusivity of solute, cm^2/s
D_o = unrestricted diffusivity of solute
K = Boltzman constant, g(cm^2)/(s^2)°K
K_d = drag coefficient, dimensionless
K_p = C_p/C_o, equilibrium partition coefficient, dimensionless
K_s = surface equilibrium constant, cm
M_t = solute uptake up to time t
M_∞ = solute uptake at equilibrium
N = Avagadro's number
P_v = pore volume, cm^3/g
r_p = pore radius, °A
r_s = solute molecular radius, °A
t = time, s
V = volume of fluid surrounding pellets, cm^3
V_m = solute molar volume at normal boiling point, cm^3/gmole
v = volume of pellets, cm^3

Greek Letters

α = ratio of volume of fluid to volume of pellets
α_n = root of $J_o(\alpha_n a) = 0$
δ = surface concentration, g/cm^2
θ = dimensionless time, $D_{\text{eff}}t/a^2$
ϵ = porosity, cm^3/cm^3
τ = tortuosity
ω = ratio of height of cylinder to diameter
η = viscosity, g/cm-s
λ = r_s/r_p, ratio of molecular radius to the average pore radius
π = 3.14159

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