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Restrictive Diffusion in Aluminas

The effect of the ratio of solute molecular diameter to the substrate pore diameter on the diffusion of polyaromatic compounds in four different pore sizes of amorphous gamma-aluminas was studied at atmospheric pressure and ambient temperature. Diffusion rates of the polyaromatic compounds in the aluminas decreased as the ratio of solute molecular diameter to pore diameter increased. Empirical correlations between the apparent reduction in solute effective diffusivity and the ratio of molecular diameter to pore diameter were obtained.

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SCOPE

Supported catalysts are normally used in upgrading of coal-derived liquids. Of primary concern is the question of whether the large, multiringed aromatic compounds found in coal-derived liquids will diffuse into the pore structure of the support to reach the active sites at sufficiently rapid rates required for an effective catalyst. When the compound molecular size becomes significant with respect to the pore size, the diffusion rate of the compound in liquid-filled pores becomes less than would be expected from an unrestricted liquid medium. If the diffusion rate of the aromatic compound is the slow step compared to the surface reaction rate, only the outer portion of the catalyst will be utilized. Therefore, knowledge of the effect of the ratio of solute molecular size to pore size on the effective diffusivity of a solute in liquid-filled pores is necessary to utilize the catalyst more effectively.

Studies on membrane diffusion (Renkin, 1954; Beck and Schultz, 1970) have clearly indicated that, by increasing the solute size, the diffusion rate of large solute molecules through certain types of membranes decreases much more rapidly than would be expected from the differences in bulk diffusivity of the solutes alone. This phenomenon has been explained on the basis of reduction of solute mobility resulting from the comparable sizes of the solute and the membrane pores, and has been called restrictive diffusion. Diffusivities of organic solutes in zeolite pores are many orders of magnitude lower than bulk values (Barrer and Brook, 1953; Ruthven and Doetsch, 1976; Satterfield and Cheng, 1972). The lowering in the diffusivities was partially credited to the restrictive effect. Due to the extremely small pore size of zeolites, the ratios of molecular size to pore size were normally greater than 0.8. At these high ratios, it was found that not only the restrictive effect slowed down the pore diffusion rate but adsorbate-adsorbent interaction and type of solvent used also affected the diffusion rate.

Few studies have been done on diffusion of polyaromatic compounds in alumina where ratios of molecular size to pore size are in the same range as those in the membrane diffusion studies. But for diffusion of polyaromatic compounds in alumina, both adsorption and diffusion occur simultaneously in the pores, whereas only diffusion takes place in the pores for the membrane diffusion system. Polyaromatic compounds are expected to be highly adsorbed by alumina. It was found that diffusion within activated carbons of highly adsorbed solutes were dominated by a surface diffusion mechanism (Fritz et al., 1981; Sudo et al., 1978).

In the present work, a systematic sorptive diffusion study of various-sized model compounds in porous alumina particles of different pore sizes was carried out. To simulate the multiringed aromatic compounds in coal-derived liquids and the supports used in the upgrading process, model polyaromatic compounds and activated aluminas were chosen for the sorptive diffusion study. The experiments involved measurement of effective diffusivities of selected polyaromatic compounds (critical molecular diameters 0.7–1.9 nm) in γ-aluminas (pore diameters 4.9–15.4 nm). The major objective was to relate the restrictive effect of pore diffusion on molecular size and alumina pore size. The work also examined a possible surface diffusion contribution.

CONCLUSIONS AND SIGNIFICANCE

Equilibrium adsorption experiments were carried out to determine the type of isotherm which was needed in the mathematical treatment of the kinetic data. Equilibrium adsorption isotherms of all the solutes were nonlinear and were well represented by Freundlich isotherms. The amount of solute uptake by alumina was shown to increase in the order of naphthalene $<$ coronene $<$ octa-ethylporphyrin $\approx$ tetra-phenylporphyrin for a given alumina.

Effective diffusivities at ambient temperature and pressure were determined by applying a pore diffusion model with a Freundlich isotherm to diffusion run data. The effective dif-

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fusivities were found to be less than the estimated pore diffusivities for nonrestrictive diffusion. The ratio of the experimental effective diffusivity to the estimated nonrestrictive pore diffusivity gave a measure of the restrictive effect due to the pores. This ratio, called the restrictive factor, was shown to decrease with increasing ratio of molecular diameter to pore diameter. The restrictive factor was substantially less than unity, even when molecular diameter was a relatively small fraction of the pore diameter. Empirical correlations between the restrictive factor and the ratio of molecular diameter to pore diameter were obtained. Surface diffusion was found not to have any significant contribution to the intraparticle diffusion.

BACKGROUND AND PREVIOUS STUDIES

For diffusion of a solute in porous materials, if the solute is relatively small compared to the pore size, the effective diffusivity of the solute is related to bulk diffusivity by the following relation (Satterfield, 1977):

$$D_e = \frac{D_b \epsilon}{\tau} \tag{1}$$

where D_e is the effective diffusivity, D_b is the bulk diffusivity in free solution, ϵ is the porosity, and τ is the tortuosity factor of the porous particle. When the solute molecular size is significant with respect to the pore size, the effective diffusivity becomes observably less than predicted by Eq. 1. A restrictive factor, $F(\lambda)$, is added to Eq. 1 to account for the reduction in diffusivity within the pore, which applies when the solute and pore size are of comparable magnitude,

$$D_e = \frac{D_b \epsilon}{\tau} \cdot F(\lambda) \tag{2}$$

$F(\lambda)$ is a function dependent on molecular size and pore size, and has a value ranging from 0 to 1.

Restricted diffusion was first observed in membrane diffusion. Several authors (Pappenheimer, 1953; Renkin, 1954) have shown that the rates of diffusion of organic nonelectrolytes through membranes with very small pores decreased as a function of molecular size far more rapidly than can be accounted for on the basis of the free diffusion coefficients of the test molecules. The prevalent explanation for restricted diffusion involves steric hindrance and hydrodynamical drag effects, as suggested by Pappenheimer (1953) and Renkin (1954). The equation describing the restrictive effect given by Renkin is,

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

where λ is the ratio of the critical molecular diameter to the pore diameter. The first term on the righthand side represents an exclusion of solute from the pores based on geometrical considerations (Ferry, 1936). The second term represents an additional hydrodynamical drag on the solute molecules as a result of the proximity of the pore walls; the function was developed by Faxen (1922) to account for the increase in drag on a sphere moving axially in a tube of comparable diameter. On the basis of this equation at a size ratio of solute to pore of 1/10, the mobility of the solute within the pore is 36% less than its mobility in free solution; about half of the restrictive effect comes from the molecular exclusion, and the other half comes from the hydrodynamical drag effect. Renkin (1954) used the above equation to fit data obtained from diffusion of water-soluble nonelectrolytes through cellulose, cellophane, and wet gel membranes. Beck and Schultz (1970) studied diffusion of several solutes with molecular diameters from 0.5 to 4.3 nm in mica membranes containing uniform, straight pores from 10 to 60 nm in diameter and 3 to 5 nm thick. Their results showed reasonable quantitative agreement with Eq. 3. Other investigators found that the hydrodynamic restricted diffusion model of Eq. 3 did not fit their data. Satterfield et al. (1973) measured effective diffusion coefficients of several nonaromatic and aromatic compounds with molecular diameters up to 1.6 nm in silica-alumina beads (pore diameter 3.2 nm). The results with the nonadsorbing solutes showed poor agreement with Eq. 3. It was suggested that the hydrodynamic-restricted diffusion model was not applicable to their study because of a breakdown in the assumption of a continuum within the pore. An empirical correlation of critical molecular diameter to pore diameter was proposed, *viz.*,

$$F(\lambda) = \frac{D_e \tau}{D_b \epsilon} = e^{-4.6\lambda} \tag{4}$$

Conlon and Craven (1972) worked on diffusion of polystyrene spheres with molecular diameters from 90 to 500 nm in a nucleopore membrane with a pore diameter of 730 nm. Results from their study also showed a restrictive effect but less than that predicted by Eq. 3. They suggested that the assumption of an acceleration-free motion of the sphere does not hold due to the random thermal motion of diffusion.

A surface diffusion mechanism was reported to significantly contribute to intraparticle transport of aromatic compounds in activated carbons by several investigators (Neretnieks, 1976b; Sudo et al., 1978). Fritz et al. (1981) reported that, by using the pore diffusion model in treating kinetic data of phenol in activated carbon, the estimated effective diffusivity was strongly dependent on concentration, the value increasing with decreasing initial concentration.

Even though the mechanism of restrictive diffusion has not yet been firmly established, the experimental results obtained from diffusion of nonabsorbing solutes in membranes (Beck and Schultz, 1970; Conlon and Craven, 1972) and silica alumina beads (Satterfield et al., 1973) clearly show the existence of a restrictive effect.

In the present work, restrictive diffusion of highly adsorbed solutes in activated aluminas was investigated. The effective diffusivities were measured using a stirred tank vessel. For a batch kinetic experiment, the concentration of solute in the liquid phase decreases due to adsorption by adsorbent. The concentration of solute in the liquid phase is measured as a function of time by an appropriate analytical technique. The rate of solute uptake depends on the rate of transport of solute from the bulk solution to the outer surface of the particles, the rate of transport into the particles and the rate of solute adsorbed on the adsorption sites. Normally, the adsorption of solute on the adsorption sites is not rate-limiting. The rate of transport to the outer surface is called external mass transfer, and the rate of transport into the particles is usually described as an intraparticle diffusion. Either or both of these rates may determine the rate of solute uptake. The external mass transfer may be determined from available correlations or may be assumed to be the fast step when sufficient mixing speed is applied. The effective diffusivity for intraparticle diffusion can then be determined by applying a proper mathematical solution of the diffusion equations to the measured uptake with time.

DATA TREATMENT

For a well-stirred batch reactor where external mass transfer is relatively fast, the governing equation for combined adsorption and diffusion in the spherical particle can be described by the following mass balance equation:

$$\epsilon \cdot \frac{\partial C_r}{\partial t} = D_e \left[\frac{\partial^2 C_r}{\partial r^2} + \frac{2}{r}\frac{\partial C_r}{\partial r}\right] - \frac{\partial q_r}{\partial t} \tag{5}$$

The initial and boundary conditions are:

$$\text{(I.C.)} \quad \text{at } t = 0, \quad C_r = 0 \quad \text{for } 0 \le r \le R \qquad (6)$$

$$\text{(B.C.)} \quad \text{at } r = 0, \quad \frac{\partial C_r}{\partial r} = 0 \quad \text{for } t > 0$$

$$\text{at } r = R, \quad C_r = C$$

and

$$V\left(\frac{\partial C}{\partial t}\right) = -4\pi R^2 N_p D_e \left(\frac{\partial C_r}{\partial r}\right)_{r=R}$$

$$C = C_o(t = 0)$$

For a nonlinear adsorption isotherm represented by a Freundlich isotherm, the relation of q and C is,

$$q = mC^{1/n} \qquad (7)$$

where m and n are constants. Solution of Eqs. 5–7 was obtained using a numerical method (Crank, 1948; Neretnieks, 1976a). Further details are given by Chantong (1982).

EXPERIMENTAL

Materials

Aromatic compounds were chosen as solutes because they strongly adsorb on alumina (Kim, 1978) and can be conveniently analysed by UV-visible spectrometry. Four aromatic compounds with critical diameters ranging from 0.7 to 1.9 nm were used in this study. The compounds were naphthalene, coronene, octa-ethylporphyrin, and tetra-phenylporphyrin, all of the highest purity commercially available. The critical molecular diameters of naphthalene (0.69 nm) and coronene (1.11 nm) were calculated from bond lengths, bond angles, and Van der Waals radii (Sutton, 1958; Pauling, 1960). Octa-ethylporphyrin (1.53 nm) and tetra-phenylporphyrin (1.9 nm) critical diameters were based on information from Fleischer (1963). Cyclohexane spectrograde was used as a solvent because its molecular size is smaller than the solutes employed; it does not adsorb strongly on alumina and it does not absorb in the UV-visible region. The cyclohexane was pretreated with calcined 13X zeolite to remove water and other impurities. Four different types of gamma-aluminas—alumina L, M, D, and C with average pore sizes of 4.9, 7.2, 9.8 and 15.4 nm, respectively—were provided by the Kaiser Aluminum Co. The physical properties of the aluminas are shown in Table 1 and the pore volume distribution in Figure 1. The aluminas were obtained in −8 + 10 mesh spherical pellets. The pellets were crushed and sieved to several sizes: −24 + 35, −35 + 65, −65 + 150, and −150 + 250 mesh (Tyler screen). The arithmetic average of the two sieve openings was taken as the particle diameters.

TABLE 1. PHYSICAL PROPERTIES OF ALUMINAS

Properties	Alumina C	D	M	L
BET Surface Area, m^2/g	200	245	320	350
Pore Volume, cm^3/g	0.77	0.60	0.58	0.43
Average Pore Diameter, nm	15.4	9.8	7.2	4.9
Particle Density, g/cm^3	1.01	1.21	1.22	1.48
Porosity	0.78	0.73	0.71	0.64

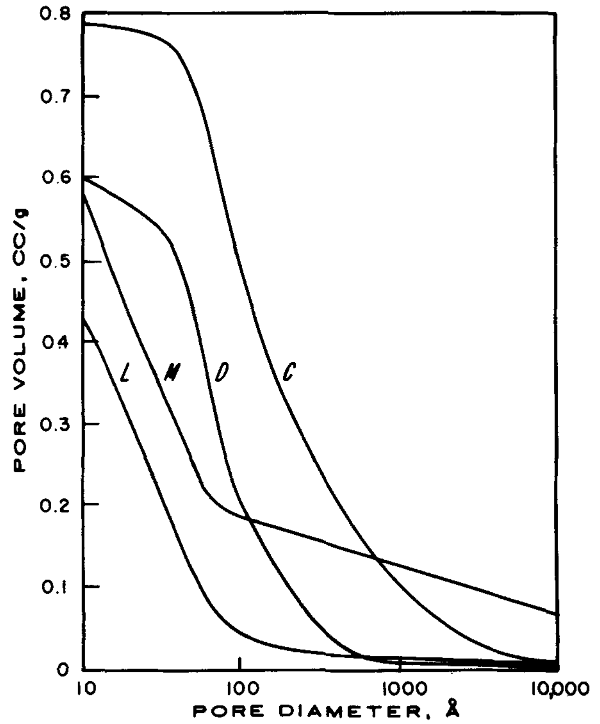
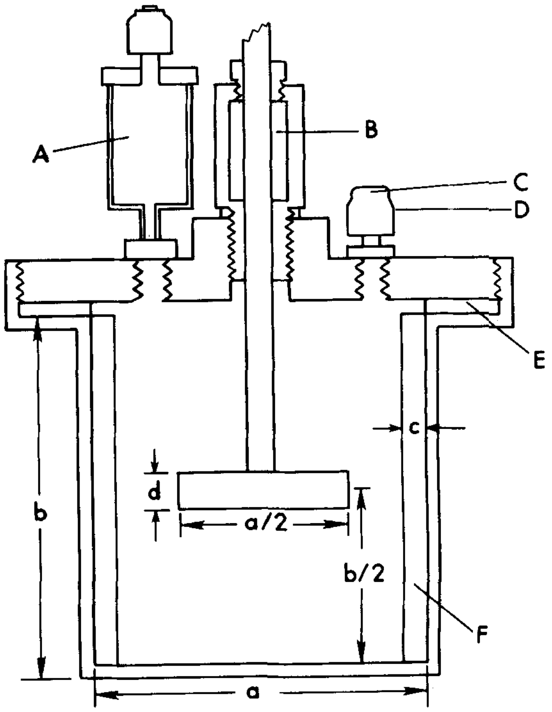


Figure 1. Pore-size distribution of aluminas (Courtesy Kaiser Alumina Co.).

Apparatus and Procedure

Two types of experiments were carried out: equilibrium adsorption uptakes and diffusion runs. Equilibrium solute uptakes for the aluminas were measured at different concentrations of solute in cyclohexane to obtain adsorption isotherms. The solution concentration range used was between 5 and 30 mg/1,000 cm^3. The aluminas of −150 + 250 mesh size were calcined in a muffle furnace at 775 K for 18 hours to remove moisture. The calcined samples were transferred directly to the solution contained in sample bottles, which had caps with Teflon liners to prevent solvent loss. The bottles were then put in a shaker contained in a constant temperature water bath at 298±1 K. Depending on the aromatic compound, the amount of the alumina used varied from 8.5 mg for octa-ethylporphyrin to 200 mg for naphthalene with 30 cm^3 solution. The alumina for each sample was weighed separately in a small crucible and all the samples for one isotherm were calcined together at the same time. After one to two weeks, depending on the size of the aromatic compounds, the concentrations of the samples were measured using a Beckman Model 25 UV-Spectrophotometer. From the initial and final concentrations, the amount of solutes taken up by the aluminas were obtained by a mass balance.

The diffusion runs were conducted in the stirred batch vessel, Figure 2. The vessel was made of stainless steel and contained four fixed baffles spaced evenly around the circumference. The vessel volume was 420 cm^3.



a	b	c	d
8 cm	8.4 cm	1/13a	1/10 a

Figure 2. Diffusion run vessel: A = moisture adsorption tube; B = Teflon packing; C = septum; D = sampling port; E = Teflon seal; and F = baffles at 90°.

Agitation was achieved with a Teflon rod connected to a variable speed motor. The vessel had a screw, airtight cover with Teflon seal. Preliminary vapor leak tests indicated no vapor loss since runs in the absence of catalyst showed no observable concentration change over 24-hour periods. Solution temperature inside the vessel was controlled by placing the vessel in a constant temperature bath held at 298±1 K. Due to the difference in sorptive diffusion rates of different solutes, different particle sizes were used in diffusion runs of different solutes to obtain a reasonable diffusion run time. Particle sizes of −8 + 10 mesh for naphthalene, −24 + 35 mesh for coronene and −35 + 65 for octa-ethylporphyrin and tetra-phenylporphyrin were used. A known weight of alumina was calcined at 775 K for 18 hours in the muffle furnace. The calcined alumina was then transferred into a 200-mesh stainless-steel gauze basket and the basket was immediately immersed into cyclohexane in order to prevent moisture uptake. A known concentration of the aromatic compound in 420 cm^3 of cyclohexane was transferred to the diffusion vessel and the stirrer operated at 600 rpm. At a given starting time, the basket containing the alumina was put into the solution in the vessel. After all the alumina particles were disengaged from the basket by agitation of the solution, the basket was removed and the vessel closed with the cap. Samples were taken periodically to monitor the change in concentration of the solution in the vessel, 2 cm^3 of solution being withdrawn for each sample. The concentrations of the samples were then measured with the UV spectrophotometer. At least seven samples were taken before 90% fractional uptake occurred. Further details are given by Chantong (1982).

RESULTS AND DISCUSSION

Equilibrium Adsorption Runs

Results from equilibrium adsorption experiments of naphthalene, coronene, octa-ethylporphyrin, and tetra-phenylporphyrin in cyclohexane with alumina D are shown in Figure 3. Uptakes for all the solutes showed a nonlinear dependence on concentration. The isotherms of the solutes with the other aluminas also showed the same nonlinear dependence. A Freundlich isotherm (Eq. 7) was used in fitting the equilibrium adsorption data. Values of the Freundlich isotherm constants for each solute-alumina pair were determined by a least-squares analysis of $\ln q_\infty$ vs. $\ln C_\infty$, Table 2. Based on the values of m and n, Table 2, the isotherm curves in Figure 3 were reconstructed using Eq. 7; the agreement with the data shows that the Freundlich isotherm is followed quite well.

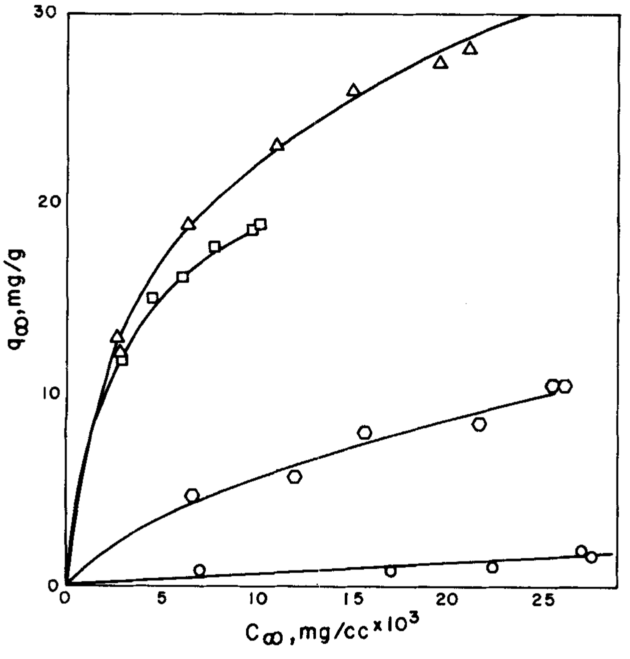


Figure 3. Equilibrium adsorption isotherms in cyclohexane with alumina D: 0 = naphthalene, ○ = coronene, □ = octa-ethylporphyrin, and △ = tetra-phenylporphyrin.

TABLE 2. FREUNDLICH ISOTHERM CONSTANTS OF MODEL AROMATIC COMPOUNDS IN CYCLOHEXANE WITH ALUMINAS

Solute	Alumina	m	n
Naphthalene	C	21.8	1.19
	D	22.3	1.26
	M	24.6	1.28
	L	22.3	1.31
Coronene	C	121.8	1.39
	D	105.8	1.57
	L	114.7	1.65
	M	114.9	1.71
Octa-Ethylporphyrin	C	72.8	3.03
	D	75.1	3.34
	M	99.2	3.51
	L	89.8	3.59
Tetra-Phenylporphyrin	C	86.1	3.16
	D	111.6	2.85
	M	122.9	2.98
	L	125.0	3.09

Equation of the Freundlich Isotherm: $q = mC^{1/n}$.

Diffusion Runs

Results from preliminary runs to check the external mass transfer resistance by varying stirring speeds and estimation of modified Sherwood number (Furusawa and Smith, 1973; Neretnieks, 1976a) showed that the external mass transfer resistance at a stirring speed at 600 rpm was negligibly small (Chantong, 1982). Diffusion runs with three different particle sizes are presented in Figure 4. The results show a dependence on the square of the reciprocal of the particle size in conformity with the rate-limiting process being due to intraparticle diffusion rather than adsorption (Foo and Rice, 1979).

The concentration changes obtained from the diffusion runs were converted to fractional approach to equilibrium $F(t)$ using the following relation:

$$F(t) = \frac{(C_o - C)}{(C_o - C_\infty)} \tag{8}$$

Incorporating Eq. 8 into the numerical solution of Eqs. 5–7 yields a value of a dimensionless time parameter, $D_e t/R^2\epsilon$, for each data point. A plot of the dimensionless time against real time should yield a straight line if the kinetics follow the pore diffusion model. Figure 5 shows such a plot for a diffusion run with tetra-phenylporphyrin. The effective diffusivity was obtained from the slope of the plot using a least-squares analysis.

In obtaining the theoretical fractional approach to equilibrium, values of the constants m and n in the Freundlich isotherm equation had to be used in the calculation. In the diffusion runs, the equilibrium solute uptake values did not always fall exactly on the equilibrium adsorption isotherm curves. Therefore, the constant m for each diffusion run was recalculated based

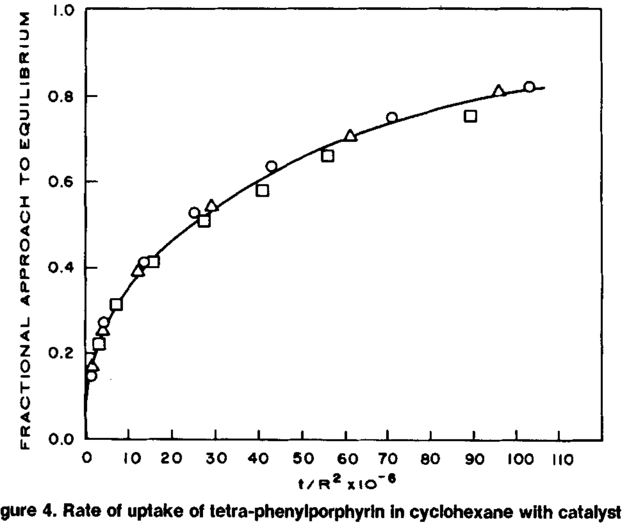


Figure 4. Rate of uptake of tetra-phenylporphyrin in cyclohexane with catalyst D vs. t/R^2 for three particle sizes: O = −60 + 100; □ = −35 + 65; △ = −25 + 35 mesh.

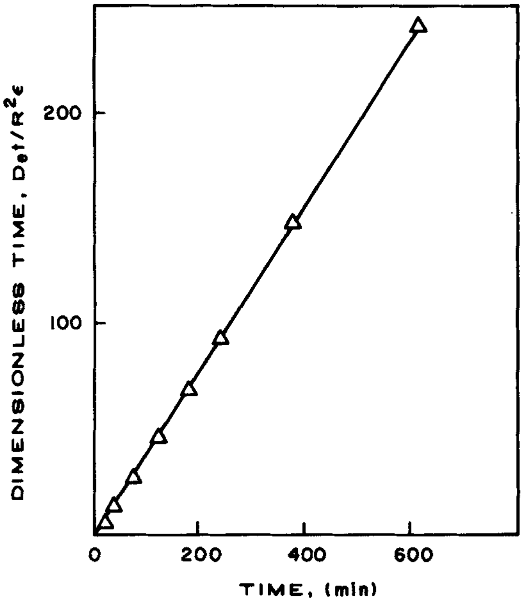


Figure 5. Fit of diffusion data to the pore diffusion model for tetra-phenylporphyrin in cyclohexane with alumina *D*.

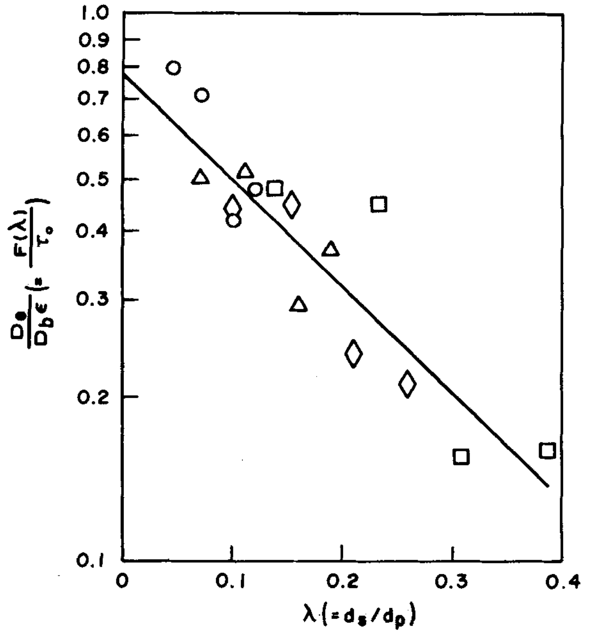


Figure 6. Semilogarithmic plot of $D_e/D_b\epsilon$ vs. λ. Alumina: ○ = C, △ = D, ◇ = M, □ = L.

on the final uptake obtained from the run and the value of n from the data of Table 2.

Effective diffusivities obtained by treating the kinetic data of the diffusion runs using the pore diffusion model with the Freundlich isotherm are shown in Table 3. For a given solute, effective diffusivity decreased in the order of alumina C > D > M > L, that is, in the order of decreasing pore size. Ratios of the effective diffusivities to the free-solution diffusivities of the same cross-sectional area ($D_b\epsilon$) are also shown in Table 3. The ratios of $D_e/D_b\epsilon$ are all less than 1, which means that the mobility of the solutes in the aluminas is less than their mobility in free-solution of the same cross-sectional area. The results show a reduction in the pore diffusion rate even at relatively low values of λ. A semilogarithmic plot of $D_e/D_b\epsilon$ vs. λ is shown in Figure 6. For a given alumina, the group parameter $D_e/D_b\epsilon$ decreases logarithmetically as the molecular size of the solute increases. Data points from the four aluminas show the same decreasing trend and agree reasonably well with each other. The nature of the different aluminas do not appear to have any significant effect on the group parameter $D_e/D_b\epsilon$. Therefore, all the data points were fitted to a straight line using a least-squares analysis. The equation of the straight line is:

$$\ln\left[\frac{F(\lambda)}{\tau}\right] = \ln\left(\frac{D_e}{D_b\epsilon}\right) = -4.5\lambda - 0.23 \qquad (9)$$

with a correlation coefficient of 0.803. As the ratio of molecular size to pore size, λ, approaches zero, $F(\lambda)$ approaches one. Therefore, from Eq. 9, the intercept of the plot corresponds to $1/\tau$. τ is calculated to be equal to 1.3. Here, τ was assumed to be the same for all the four aluminas. According to the random pore model, the tortuosity values of the aluminas used in this study would be between 1.28 – 1.56 (Satterfield, 1977). The value of τ obtained from the intercept of the plot is the tortuosity value when the ratio of diffusing molecular size to pore size approaches zero. Therefore, τ_o is used instead of τ. If the tortuosity is not constant but is a function of the molecular size of the diffusing molecule (Schultz and Gerhardt, 1969; Beck and Schultz, 1972), an increase in tortuosity with molecular size would be included in $F(\lambda)$. Equation 9 can be rearranged into a general form,

$$F(\lambda) = \frac{D_e\tau_o}{D_b\epsilon} = 1.03e^{-4.5\lambda} \qquad (10)$$

Equation 10 represents a simple empirical correlation between the reduction in diffusion rate of a solute with the ratio of solute molecular size to pore size. The equation should be valid for the range of λ less than 0.4 where the experiments were carried out.

Another form of empirical equation suggested by Beck and Schultz (1970) is,

$$F(\lambda) = (1 - \lambda)^z. \qquad (11)$$

A logarithmic plot of $D_e/D_b\epsilon$ vs. $(1 - \lambda)$ should yield a straight line with slope equal to z and intercept corresponding to $1/\tau_o$. Such a plot is shown in Figure 7. A correlation coefficient of 0.777 was obtained, showing this

TABLE 3. EFFECTIVE DIFFUSIVITIES OF AROMATIC COMPOUNDS IN CYCLOHEXANE WITH ALUMINAS

Solute	$D_b \times 10^6$*, cm²/s	Alumina	$\lambda = \left(\frac{d_s}{d_p}\right)$	$D_e \times 10^6$, cm²/s	$\frac{D_e}{D_b\epsilon}$
Naphthalene	11.20	C	0.045	6.95	0.80
		D	0.07	4.08	0.50
		M	0.10	3.45	0.43
		L	0.14	3.40	0.47
Coronene	7.45	C	0.07	4.14	0.71
		D	0.11	2.82	0.52
		M	0.15	2.36	0.45
		L	0.23	2.11	0.44
Octa-Ethylporphyrin	4.36	C	0.10	1.42	0.42
		D	0.16	0.94	0.29
		M	0.21	0.73	0.24
		L	0.31	0.43	0.15
Tetra-Phenylporphyrin	4.37	C	0.12	1.61	0.47
		D	0.19	1.20	0.38
		M	0.26	0.66	0.21
		L	0.39	0.47	0.17

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* Values estimated using Wilke-Chang equation (Reid et al., 1977).

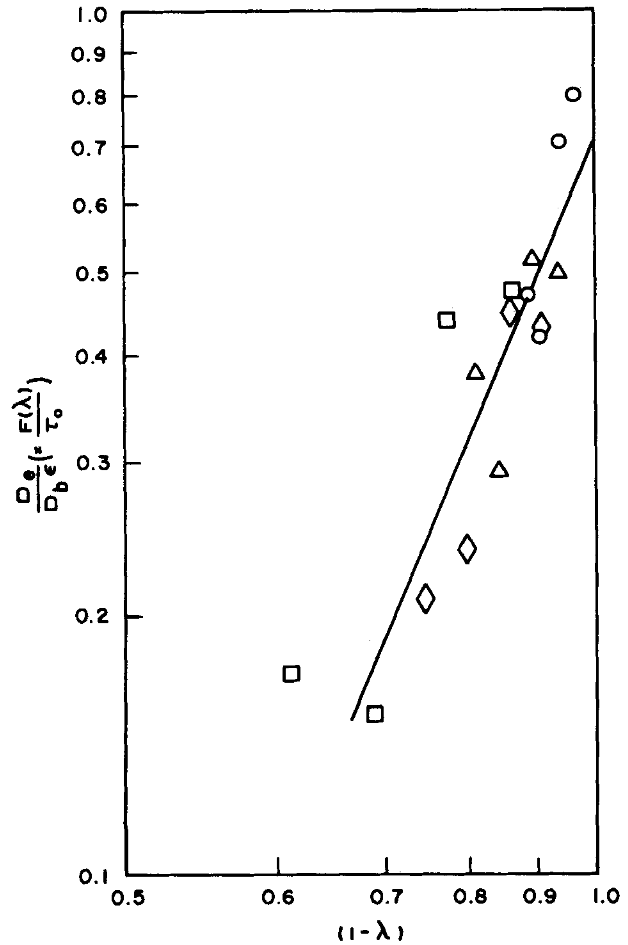

Figure 7. Logarithmic plot of $D_e/D_b\epsilon$ vs. (1 − λ). Alumina: O = C, Δ = D, ◇ = M, □ = L.

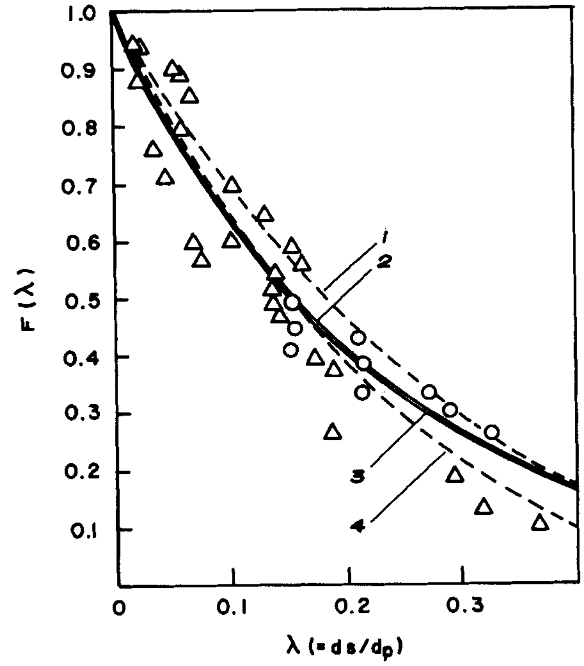

Figure 8. Comparison of results from this study (lines) with literature data. Numbers represent equations: (1) 10, (2) 12, (3) 4, (4) 3. O = Satterfield et al. (1973); Δ = Beck and Schultz (1970).

Table 4. Concentration Effect on Effective Diffusivity of Tetra-Phenylporphyrin with Alumina C

Initial Concentration $C_o \times 10^3$, mg/cm³	Final Concentration $C_\infty \times 10^3$, mg/cm³	$D_e \times 10^6$, cm²/s	$\left(\frac{\partial q}{\partial C}\right)_{C=C_\infty}$
14.7	8.8	1.62	1,684
29.9	21.6	1.70	986

relationship to be slightly poorer than for Eq. 9. A z value of 3.5 and τ_o of 1.4 are obtained from a least-squares analysis of this plot. Again, a reasonable value of τ_o is obtained. The empirical correlation for the restrictive factor is, therefore,

$$F(\lambda) = (1 - \lambda)^{3.5} \tag{12}$$

A value of 4 for z was used by Beck and Schultz to correlate their membrane diffusion data.

In Figure 8, the correlations of Eqs. 10 and 12 are compared with Beck and Schultz's results (1970) from membrane diffusion and Satterfield et al. (1973)'s results from diffusion of nonadsorbing solutes with silica-alumina. The Renkin equation (Eq. 3) used by Beck and Schultz to fit their data and the empirical correlation proposed by Satterfield et al. (Eq. 4) are also shown in Figure 8. As can be seen, the correlations from the present study agree reasonably well with results of these investigators. Equation 12 predicts a slightly higher value of $F(\lambda)$ than Eq. 10, but the difference is small and within the scatter of the experimental data. The general agreement between these sets of data is somewhat surprising, since quite different systems were studied. Beck and Schultz used mica membranes with nonadsorbing solutes, Satterfield used a silica alumina catalyst with nonadsorbing solutes, and in the present study highly preferentially adsorbed solutes with gamma aluminas were used. Thus, it appears that the restrictive diffusion correlations of Eq. 10 or 12 are general ones that may apply to all systems.

When both surface and pore diffusion contribute to the internal diffusion, the effective diffusivity is expressed as (Komiyama and Smith, 1974; Chantong, 1982):

$$D_e = \frac{D_b\epsilon}{\tau} + \rho D_s \frac{\partial q}{\partial C} \tag{13}$$

Here, $D_b\epsilon/\tau$ is the pore diffusion term and $\partial q/\partial C$ is the slope of the isotherm. For a nonlinear isotherm, $\partial q/\partial C$ is higher at low concentrations. From Eq. 13, as $\partial q/\partial C$ increases with decreasing concentration, D_e should also increase. Effective diffusivities of tetra-phenylporphyrin in cyclohexane with alumina C at two different concentrations are shown in Table 4. The isotherm for tetra-phenylporphyrin with alumina C is nonlinear, giving the values of $\partial q/\partial C$ shown in Table 4. However, the values of D_e were not affected by the difference in $\partial q/\partial C$ values showing that Eq. 13 does not apply to this system. Furthermore, the estimated effective diffusivity using the pore diffusion model was found to be independent of concentration (Chantong, 1982). Therefore, it can be concluded that surface diffusion does not significantly occur in the systems studied here.

Even though the mechanism of restrictive diffusion has not yet been firmly established, the experimental results obtained here clearly show that the mobility of molecules through comparative size pores is significantly less than their mobility through free solution of comparable cross-sectional area. The decrease in mobility is related to the ratio of molecular size to pore size. If it is assumed that the same empirical correlations apply under hydroprocessing conditions, they can be useful for predictions of diffusion in porous catalysts, which are essential in designing optimal pore size catalysts for upgrading of heavy feedstocks (Spry and Sawyer, 1975; Rajagopalan and Luss, 1979). Further work at higher temperature and pressure is needed to confirm this assumption.

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NOTATION

C = average bulk solute concentration at time t, mg/cm³
C_o = initial bulk concentration, mg/cm³
C_r = solute concentration within particle pores at radius r, mg/cm³
C_∞ = equilibrium concentration of bulk solution, mg/cm³
d_p = average pore diameter, nm
d_s = solute critical molecular diameter, nm
D_b = bulk diffusivity, cm²/s
D_e = effective diffusivity, cm²/s
$F(t)$ = fractional approach to equilibrium
$F(\lambda)$ = restrictive factor
m = constant in Freundlich isotherm equation
n = constant in Freundlich isotherm equation

N_p = number of particles
q = total amount solute adsorbed at time t, mg/g
q_r = amount solute adsorbed at radius r, mg/g
q_∞ = amount solute adsorbed at equilibrium, mg/g
r = radial coordinate, cm
R = average particle radius, cm
t = time, s
V = total volume of liquid solution, cm^3

Greek Letters

ϵ = particle porosity
λ = ratio of solute critical molecular diameter to pore diameter ($= d_s/d_p$)
ρ = particle density, g/cm^3
τ = tortuosity factor of porous particles
τ_o = tortuosity factor of porous particles when the ratio of diffusing molecular size to pore size approaches zero

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