NOTATION

C = concentration, mole/cm^3
$\mathfrak{D}_J$ = diffusivity of species J, cm^2/s
E = electrode potential vs. N.H.E., Volts
E_A = activation energy, Joule/mole
F = Faraday's constant, A·s/equiv
$\Delta H_o^{\neq}$ = activation enthalpy, Joule/mole
h = electrochemical Thiele modulus
$\bar{i}$ = current density, A/cm^2
j = reaction order of species J
k_J^0 = rate constant at zero potential, mole^{1-j}·cm^{3j-2}·s^{-1}
L = electroactive pore length, cm
N_p = number of pores per unit area
n = number of electrons
R_p = pore radius, cm
$\mathcal{R}$ = gas constant, Joule/mole °K
$\bar{r}_J$ = reaction rate of species J, mole/cm^2·s
T = temperature, °K
X = axial distance, cm

α = transfer coefficient
ϵ = electrochemical effectiveness factor
$$= -\frac{1}{h^2}\left(\frac{d\theta_J}{dX^*}\right)_{X^*=0}$$
θ = dimensionless concentration ($= C_J/C_{J_\infty}$)

Subscripts

g = observed value, Equation (6)
J = species J
∞ = intrinsic or bulk solution value

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Restricted Diffusion of Liquids in Microporous Catalysts

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The problem of diffusion of liquid molecules in microporous catalysts and other porous material remains a difficult one in terms of relating effective diffusivities with the variables involved. Though there is a general concensus that there is a hindrance to transport of molecules in pores of finite width, the mechanisms contributing to this hindrance are not well understood. Even diffusivity data for molecules in porous media, though few in number, generally vary in magnitude because of the different set of assumptions and conditions under which experimental transport data are analyzed, and also due to difficulties in obtaining reliable measurements of low concentrations, very often in parts per million.

Several groups of workers have attempted to derive quantitative expressions for hindered diffusion in pores. Ferry (1936) proposed that hindered diffusion occurs because of the exclusion of molecules due to statistical effects related to the relative size of molecules to the pore. Ferry pictured the molecule as being reflected from the pore mouth if it is within a distance of less than one molecular radius from the pore wall. Recent theories (Ackers, 1970) derived from ideas in exclusion gel permeation chromatography related hindered diffusion to the exclusion phenomenon, which simply states in geometric terms that the equilibrium partition coefficient is given by

$$K_p = C_p/C_o = (1 - \lambda)^2 \qquad (1)$$

The geometric exclusion hypothesis neglects the very real effect of surface adsorption within the pore or the opposite effect of repulsion between molecule and surface. The magnitude of the adsorption or repulsion depends on the chemical and electrical properties of the surface and the solute molecules.

Subsequent efforts in development of a model to describe hindered diffusion was done by postulating a hydrodynamic drag effect (Friedman and Kramer, 1930; Faxen, 1973; Lane, 1950). However, neither of these adequately explained the reduction in effective diffusivity through porous material. Pappenheimer et al. (1951) and Renkin (1954) suggested the combination of the two effects to give

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$$D_{eff} = D_o(1-\lambda)^2[1 - 2.104\,\lambda + 2.09\,\lambda^2 - 0.95\,\lambda^3] \tag{2}$$

This expression has been used by Beck and Schultz (1972) to show satisfactory agreement with their data but was found to be less or not satisfactory by other workers (Satterfield et al., 1973; Prasher and Ma, 1977; Malone and Anderson, 1977). Similar models of this type have been derived by Happel and Brenner (1965) and by Brenner and Gaydos (1977).

Very recently, Anderson and Quinn (1974) and Malone and Anderson (1977) suggested that the reduced diffusivity (D_{eff}/D_o) can be approximated by

$$\frac{D_{eff}}{D_o} = K_p K_d \tag{3}$$

For molecules approaching the shape of a rigid sphere, $K_p = (1-\lambda)^2$, and K_d given by the expression by Brenner and Gaydos (1977) would give

$$\frac{D_{eff}}{D_o} = 1 + \frac{9}{8}\lambda \ln \lambda - 1.539\,\lambda + 0(\lambda^2) \tag{4}$$

There are difficulties in accepting this expression. The obvious one is that experimental data would contradict this. According to this theory, the pore diffusivity is directly proportional to the equilibrium partition coefficient. Experimental data by Satterfield et al. (1973) and Prasher and Ma (1977) would suggest completely the opposite. Also, the equilibrium partition coefficient for a molecule approaching the shape of a rigid sphere as predicted by their model λ is always less than 1.0, but experimental data from the recent studies just cited indicate that the partition coefficient in the case of at least molecules having $\lambda < 0.3$ depends more on the specific interaction between molecule and surface than on λ itself. Thus, K_p values between 1.0 and 4 seem to be quite common, and higher values than these have also been reported.

In this study, further experimental data for transient diffusion and adsorption with respect to two different alumina catalysts is reported. The data are analyzed on the basis of the diffusion model proposed in the recent study by Prasher and Ma (1977).

EXPERIMENT

Materials

The two samples of catalyst pellets used in this study are γ alumina catalyst pellets. The average pore radius based on pore volume for WP-3 is 48.5Å (4.85 nm) and that for WP-4 is 77Å (7.7 nm). The pore volumes are 0.626 and 0.58 cm³/g of catalyst for WP-3 and WP-4, respectively. The pellets as received are cylindrical in shape. WP-3 has an average diameter of about 0.33 cm, while WP-4 has an average diameter of about 0.16 cm. Since the rate of mass fractional uptake of solute in the system is dependent also on the ratio of pellet length to pellet diameter, for the case of the diffusion experiments the pellets are chosen in such a way that the ratio of the length to diameter ω varied only by ± 5 to 10% from the average value of ω.

Solute-solvent systems covering a wide array of substituted aromatic, aliphatic, and olefin compounds were chosen as shown in Table 1. Reagent grade chemicals were used in most cases, but in cases where they were not available, chemicals with a purity in excess of 99% were used. The average molecular radii for these compounds were calculated from the molar volumes of the compounds at their boiling point by assuming the molecules to be spheres.

Apparatus and Procedures

In the transient diffusion experiments, the catalyst pellets are first equilibrated with about 10% solute-solvent mixture for a day or more in two carrier baskets which are placed in an agitated reactor at the beginning of the transient desorption experiment. Before equilibration with the solute-solvent solution, the pellets are first activated by heating to 150°C for several hours to remove moisture from the surface. The reactor is equipped with an impeller with a carrier on which the two baskets can be implaced. Most experiments take between ½ to 2 hr to accomplish complete solute uptake to equilibrium. At periodic intervals, small samples are withdrawn to monitor the fractional uptake of the solute.

For equilibrium adsorption studies, known concentrations of solute and known amounts of solution (usually 3 to 4 g) are equilibrated with about 1 to 1½ g of activated catalysts for about a day in air tight bottles. The bottles

TABLE 1. DIFFUSION AND ADSORPTION DATA FOR CATALYSTS

WP-3	Solute	Solvent	λ	$D_o \times 10^5$ cm²/s	$D_{eff} \times 10^5$ cm²/s	K_p	$D_{eff} K_p \tau / D_o$
1	1,3,5-triisopropylbenzene	Cyclohexane	0.101	0.758	0.129	1.11	0.297
2	Mesitylene	Cyclohexane	0.0827	1.09	0.392	1.04	0.589
3	1-hexene	Toluene	0.0774	2.03	0.572	0.900	0.399
4	1,3,5-triethylbenzene	Cyclohexane	0.0927	0.884	0.202	1.06	0.381
5	2,2,4-trimethylpentane	Toluene	0.0862	1.67	0.471	0.386	0.371
6	1-decene	Benzene	0.0917	1.26	0.381	0.736	0.350
7	o-terphenyl	Cyclohexane	0.0983	0.795	0.103	1.45	0.296
8	1-octene	Benzene	0.0852	1.44	0.407	0.850	0.378
9	1,2-diphenylethane	Cyclohexane	0.0927	0.884	0.128	1.70	0.388
10	1-methylnaphthalene	Cyclohexane	0.0840	1.06	0.259	1.25	0.481
11	n-undecane	Benzene	0.0956	1.17	0.276	0.804	0.299
12	n-hexane	Benzene	0.0787	1.66	0.474	0.900	0.405
13	n-dodecane	Benzene	0.0983	1.44	0.350	0.651	0.323
WP-4							
1	1-methylnaphthalene	Cyclohexane	0.0528	1.06	0.402	1.37	0.830
2	Mesitylene	Cyclohexane	0.0521	1.09	0.585	1.06	0.906
3	1-hexene	Toluene	0.0487	2.03	0.606	2.37	1.13
4	Tetralin	Cyclohexane	0.0520	1.09	0.691	0.754	0.761
5	1,3,5-triethylbenzene	Cyclohexane	0.0588	0.884	0.455	1.10	0.902
6	1,3,5-triisopropylbenzene	Cyclohexane	0.0636	0.758	0.274	1.15	0.662
7	Methylcyclohexane	Toluene	0.0496	1.97	0.725	1.05	0.615
8	Acenaphthene	Benzene	0.0532	1.47	0.612	1.09	0.722

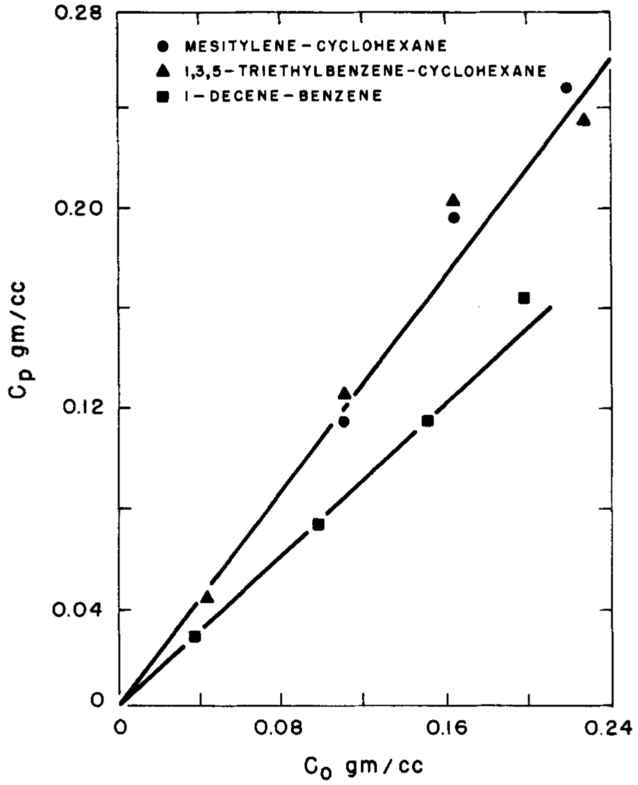

Fig. 1. Typical adsorption isotherms for WP-3 catalyst.

are placed in a constant temperature water bath and are shaken periodically to hasten equilibrium.

For the case of a finite cylinder in an infinite medium, the numerical solutions to the two-dimensional diffusion equation (Ma and Evans, 1968; Prasher and Ma, 1977) was used to evaluate effective diffusivities. Further details on the diffusion and adsorption experiments, calculations, and methods of analysis can be obtained from Prasher and Ma (1977).

RESULTS AND DISCUSSION

Equilibrium Studies

Table 1 gives the average values of the partition coefficients for the solute-solvent-catalyst system studied. Figure 1 represents typical plots for a few of these adsorption systems studied. As can be seen from Figure 1, the adsorption isotherms for these systems are linear. Also, from the values reported in Table 1, it is clear that the partition coefficients range from about 0.6 to 2 in value. These values are quite different from the predictions based on steric exclusion of molecules in pores. Several studies involving the partitioning of macromolecules in membranes and other porous media, for example, the partitioning of protein molecules, polymer, and latex molecules (Ackers, 1964; Yau, 1969; Colton et al., 1971, 1975) report a partitioning effect due to exclusion because λ (the ratio of molecular radius to pore radius) is large. These values are generally consistent with and approximate the values given by Equation (1), though the method of computing λ may vary in each case.

The data obtained in this study, where λ values are generally less than $\lambda = 0.15$, strongly suggest that K_p values are only, if at all, minimally influenced by λ. The predominating effect is the specific surface to molecule effect, or, putting it another way, the electronic forces between molecule and surface definitely affect K_p more strongly than any geometrical consideration. Thus, the data presented for the two alumina catalysts show that the substituted single and double ring aromatic solutes are more strongly adsorbed than the naphthenic solvent used and hence have K_p values of one or greater though these molecules are larger than the naphthenic solvent. Similarly, it is observed that the adsorption of *o*-terphenyl, 1,2-dibenzylethane, and 1-methylnaphthalene on WP-3 (all having larger molecular radii than their corresponding

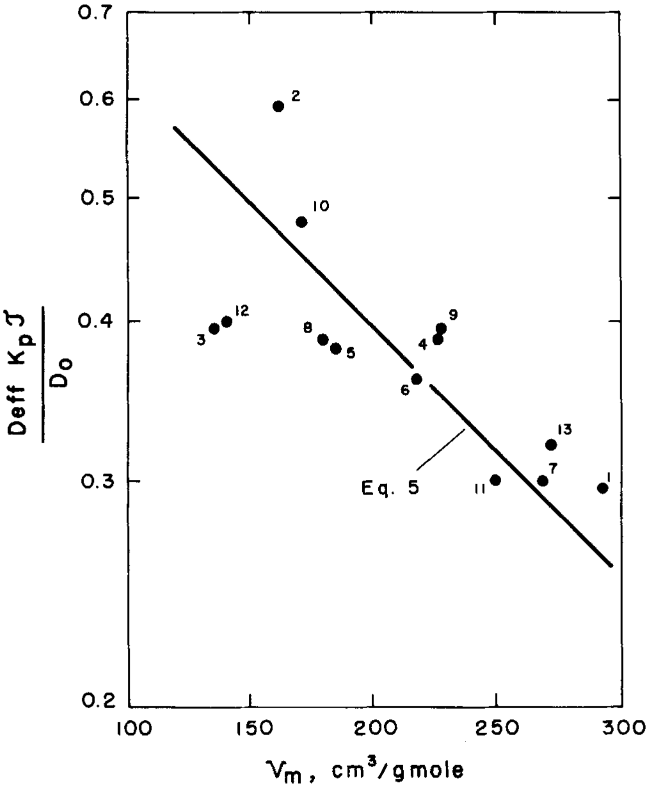

Fig. 2. Reduced diffusivity vs. molar volume of solutes in WP-3 catalysts.

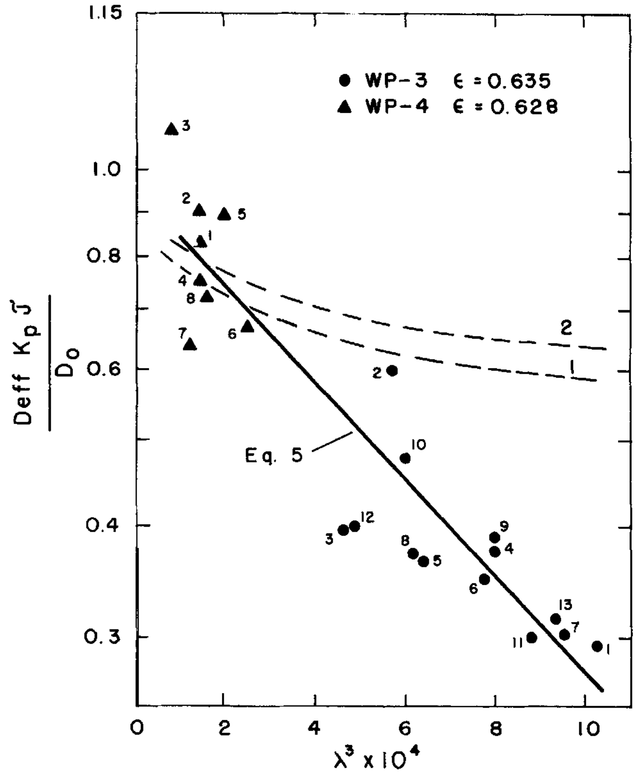

Fig. 3. Correlation for effective diffusivity in catalysts. 1. Malone and Anderson (1977) rigid sphere model. 2. Renkin equation.

solvents) have considerably larger partition coefficients than 1.0. On the other hand, the straight chain compounds (olefins and paraffins) in the case of WP-3 yielded K_p values less than 1.0 when used with aromatic solvents. In the case of the paraffins, this is to be expected, though the values obtained for the olefins are somewhat unexpected.

The proposition put here that the adsorption isotherm for any solute-solvent-adsorbent system is primarily dependent on the physicochemical interaction is supported by the data of Satterfield et al. (1973). They reported K_p values of around four and in some cases substantially higher than four for the adsorption of substituted aromatics on silica-alumina using saturated hydrocarbon as solvent. They also reported values of $K_p = 1$ for n-paraffins. The values of λ obtained in their study are between 0.15 and 0.5.

Diffusion of Molecules with Preferential Adsorption of Solute or Solvent

The effective diffusivity values obtained in this study with respect to a host of solute-solvent systems and the two catalysts very definitely tie effective diffusivity values to the partition coefficient K_p and also the ratio of the molecular radius to the average pore radius. The values of effective diffusivity show approximately an inverse relationship to the partition coefficient. Figure 2 is a semilog plot of the reduced diffusivity ($D_{\text{eff}}K_p\tau/D_o$) vs. the molar volume of solute in WP-3. As shown by this figure, there is a linear relationship between the reduced diffusivity and the molar volume of the solute. In line with another study (Prasher and Ma, 1977), a linear regression of the data for the two sets of data for WP-3 and WP-4, respectively, yielded a very significant semiempirical relationship of the form (Figure 3)

$$\ln \frac{D_{\text{eff}}K_p\tau}{D_o} = b\lambda^3 + a \tag{5}$$

The values of the constants a and b within the 95% confidence interval are found to be

$$a = 0.0575 \pm 0.147$$

$$b = 1241.8 \pm 242.4$$

τ is estimated from the random pore model. It has been suggested that the concept of τ is more complicated than the inverse relationship suggested by the random pore model (van Brakel and Heertjes, 1974), and actual values may be different from those predicted by the random pore model. The average deviation of the data is less than 15%, and this indicates the data as a whole seem to be excellent. The intercept value of $D_{\text{eff}}\tau K_p/D_o$ as $\lambda \rightarrow 0$ is 0.94, and the regression value of the inverse natural log of a within the 95% confidence interval is given by

$$0.815 \leq \text{anti-ln}\ a \leq 1.09 \tag{6}$$

The fact that reduced diffusivity value is close to 1.0 as $\lambda \rightarrow 0$ indicates indirectly that the deduction of the diffusion mechanism by the set of equations used in describing the model is at least approximately correct.

The data presented in an earlier study (Prasher and Ma, 1977) is of the same order as the data submitted in this study and shows a correlation having the same form as the one obtained in this study. However, the spread of the pore size distribution for the porous material used in the previous study is relatively large.

Beck and Schultz (1972), using Renkin's equation for reduced diffusivity, showed that when σ/r_p is equal to 0.5 or higher, the reduced diffusivity could vary greatly from the prediction based on $\sigma/r_p = 0.2$, which deviates almost indistinguishably at low λ from one based on $\sigma/r_p = 0$. This partly explains the difference in the constants evolved in these two studies. Pending the accumulation of a wider distribution of data involving different pore size distribution of porous media, a comprehensive model is not attempted at the present time.

The reduced diffusivity data reported here is of the same order as that reported by Malone and Anderson (1977), though the data of Malone and Anderson on the diffusion of charged latex particles in mica pores seem to be about 30 to 50% lower than the correlation obtained here. Their reduced diffusivity values, however, abruptly approach zero in the range of $0.1 < \lambda < 0.2$. However, it must be pointed out they did not report independent measurements of K_p but assumed that K_p conforms to the value given in Equation (1). Beck and Schultz (1972) also recently reported reduced diffusivity data which correlates well with the Renkin equation. Again, their work involving the diffusion of sugars and urea under pseudo steady state conditions in mica pores did not take into account the possibility that K_p could vary substantially from values predicted by the exclusion effect.

The model proposed by Malone and Anderson (1977) on the effect of K_p contradicts the data reported earlier by Satterfield et al. (1973), Prasher and Ma (1977), and the present study. In this particular respect, the model proposed for the effective diffusivity in this study is radically different than those hypothesized in other studies. Also, as conceived by evidence from this work, the partition coefficient would definitely affect the observed effective diffusivity values in the case of transient processes in the pellet.

CONCLUSIONS

1. On the basis of this work and other recent work, the effective diffusivity for transient diffusion processes in liquid diffusion in catalysts is inversely proportional to the partition coefficient.
2. In the range $\lambda < 0.1$, at least the reduced diffusivity can be empirically related to an exponential type relationship in λ^3.

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NOTATION

a = constant in Equation (5), also radius of cylindrical pellet
b = constant in Equation (5)
C = solute concentration, g/cm^3
C_o = bulk solute concentration at equilibrium, g/cm^3
C_p = solute concentration in pores, 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, cm^2/s
K_d = drag coefficient, dimensionless
K_p = C_p/C_o, equilibrium partition coefficient, dimensionless
r_p = pore radius, Å
r_s = solute molecular radius, Å
V_m = solute molar volume at normal boiling point, cm^3/gmole
ϵ = porosity, cm^3/cm^3
τ = tortuosity
λ = r_s/r_p, ratio of molecular radius to the average pore radius

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Gas Solubilities Near the Solvent Critical Point

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An estimation of gas solubilities in liquids at high temperatures is required for a number of industrial process calculations and geological investigations. Few experimental data, however, are available, and such a lack of information has justified attempts of extrapolations by means of correlations (Hayduck and Laudie, 1973; Cysewski and Prausnitz, 1976; de Ligny et al., 1976). Extrapolations to high temperatures can be subject to large errors, mainly owing to the presence of a minimum in the variation of solubilities with temperature. Here a limiting condition based on thermodynamics is found. All correlations must be consistent with this limit in order to allow reasonable estimations.

Hayduk and Laudie (1973) observed that all gas solubilities in a given solvent have a common value as the solvent critical temperature is approached. Extrapolating bilogarithmic curves of gas solubilities vs. temperature to the solvent critical temperature, they determined reference solubilities in a number of polar and apolar solvents. It is shown here that their observation is true for all gases and solvents, and an exact value of the reference solubility is derived from thermodynamic considerations. It is also shown that enthalpies of solution of all gases are infinite at the solvent critical temperature.

THERMODYNAMIC FRAMEWORK

Let the solubility of a gas (2) in a solvent (1) at a given temperature T be defined as follows:

$$S_{21} = \lim_{x_2 \to 0} \left(\frac{x_2}{P y_2} \right) \tag{1}$$

The fugacity of the gas in the liquid phase can be written as

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