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Effect of Pressure and Temperature on Restrictive Diffusion of Solutes in Aluminas

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PREVIOUS STUDIES

Previous studies of the diffusion of molecules in porous solids have been recently reviewed (Chantong, 1982). These studies have shown that when the critical molecular diameter of the diffusing molecule is an appreciable fraction of the pore diameter of the solid, diffusion is retarded from that of normal pore diffusion. The phenomenon has been termed "restrictive diffusion" and has been explained on the basis of steric hindrance and hydrodynamical drag effects.

On the basis of diffusion measurements of various molecules in silica-alumina beads, Satterfield et al. (1973) have derived an empirical equation relating the critical molecular diameter to pore diameter, λ, as:

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

Later studies by Chantong and Massoth (1983) with polyaromatic compounds in aluminas gave a similar relationship, *viz.*,

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

confirming the general validity of this form for adsorbing and nonadsorbing solutes. In this study, we report data on the effects of pressure and temperature on the restrictive factor.

EXPERIMENTAL

Three different aluminas were used, having average pore diameters: C-15.4 nm, M-7.2 nm, and L-4.9 nm. Other physical properties of the aluminas are given by Chantong and Massoth (1983). The aluminas were crushed and sieved to give fractions among 0.417–0.701 mm, 0.208–0.417 mm, and 0.104–0.208 mm. The arithmetic average of the two values was taken as the particle diameters. Coronene (Aldrich), octaethylporphyrin (Man-Win), and tetraphenylporphyrin (Aldrich) were used as adsorbates. Their critical diameters are: 1.11 nm, 1.53 nm and 1.9 nm, respectively. n-Dodecane (Aldrich, 99%) was employed as solvent for higher temperature runs because of its low vapor pressure, and n-decane (Aldrich, 99+%) and cyclohexane (Matheson, Coleman and Bell, spectrograde) were used in the high pressure experiments at ambient temperature. All solvents were treated with calcined molecular sieve to remove water and other impurities.

A 1-L packless autoclave with Magnedrive assembly was used for the diffusion studies. A known weight of alumina, calcined at 773 K for 18 hours, was rapidly transferred to a fine-mesh stainless steel gauze basket and the basket immediately immersed into the solvent in order to prevent moisture pickup. A solution of known concentration of the aromatic compound in 500 cm^3 was prepared and transferred to the autoclave. The stirrer was then turned on and operated at 600 rpm. Above 500 rpm, measured diffusivities were not affected by stirring speed (Chantong, 1982). Molecular sieve 5A (~0.5 g), calcined at 523 K for 4 hours, was added to the solution and stirred at the given temperature for overnight to remove interfering materials.

At a given starting time, the basket containing the alumina was removed from the solvent and placed in the solution in the reactor. Samples (2 cm^3) were taken periodically and analyzed using a Beckman Model 25 UV-VIS spectrometer at 328.8 nm for coronene, at 498.7 nm for octaethylporphyrin and at 512.4 nm for tetraphenylporphyrin. As there was an appearance of chemical reaction of tetraphenylporphyrin at 363 K during the diffusion experiment, the upper temperature was confined to 333 K.

Effective diffusivities were determined from the uptake data by applying a pore diffusion model described previously (Chantong and Massoth, 1983). However, since reproducible isotherms at elevated temperatures could not be obtained, a linear isotherm was used in all diffusivity calculations.

RESULTS AND DISCUSSION

No significant effect of helium pressure on effective diffusivities of the solutes was observed at 7.0 MPa. There was also no difference

TABLE 1. EFFECT OF H_2 PRESSURE ON EFFECTIVE DIFFUSIVITIES OF CORONENE IN ALUMINA C AND L AT 298 K

	D_e, cm^2/s					
Alumina	C		C		L	
Solvent	n-decane		cyclohexane		cyclohexane	
Pres., MPa	0.29	7.0	0.085	7.0	0.29	7.0
$D_e \times 10^6$, cm^2/s	4.9	4.7	4.1	4.3	3.8	3.7

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TABLE 2. EFFECT OF TEMPERATURE ON EFFECTIVE DIFFUSIVITIES

		Coronene			Octaethylprophyrin			Tetraphenylporphyrin		
Alumina	Temp., K	$D_b \times 10^6$ cm^2/s	$D_e \times 10^6$ cm^2/s	$D_e/D_b\epsilon$	$D_b \times 10^6$ cm^2/s	$D_e \times 10^6$ cm^2/s	$D_e/D_b\epsilon$	$D_b \times 10^6$ cm^2/s	$D_e \times 10^6$ cm^2/s	$D_e/D_b\epsilon$
C	298	6.7	2.4	0.46	4.1	1.34	0.42	4.0	0.81	0.25
	313	8.9	4.8	0.69	5.4	1.54	0.36	5.4	1.4	0.32
	333	12.5	6.7	0.69	7.6	2.20	0.36	7.5	2.7	0.46
M	298	6.7	1.1	0.23	4.1	0.64	0.22	4.0	0.66	0.23
	313	8.9	3.1	0.49	5.4	1.01	0.26	5.4	1.00	0.26
	333	12.5	5.1	0.57	7.6	1.34	0.26	7.5	1.9	0.35
L	298	6.7	0.63	0.15	4.1	0.31	0.14	4.0	0.35	0.14
	313	8.9	1.2	0.20	5.4	0.70	0.20	5.4	0.59	0.17
	333	12.5	2.6	0.33	7.6	1.04	0.22	7.5	1.4	0.28

in effective diffusivities up to 7.0 MPa of hydrogen, Table 1. The same results were observed regardless of the alumina or solute use. Although liquid viscosity increases with pressure (Reid et al., 1977) and liquid bulk diffusivity decreases with an increase in viscosity, the effect is very small, and diffusivities were not noticeably affected by pressure.

Effective diffusivities of coronene, octaethylporphyrin and tetraphenylporphyrin in aluminas at 298, 313, and 333 K are presented in Table 2. Bulk diffusivities increase with temperature. But the increase in effective diffusivities were higher than the bulk diffusivities.

Ratios of $D_e/D_b\epsilon$ were previously correlated with a restrictive factor $F(\lambda)$ (Chantong and Massoth, 1983), *viz.*,

$$D_e/D_b\epsilon = F(\lambda)/\tau_o. \qquad (1)$$

From a semilogarithmic plot of $D_e/D_b\epsilon$ vs. λ, a straight line equation was derived for alumina at ambient temperature, which has the form:

$$ln(D_e/D_b\epsilon) = -\alpha\lambda - ln\,\tau_o \qquad (2)$$

where α is the slope of the plot. Plots of $ln(D_e/D_b\epsilon)$ vs. λ for the present data are shown in Figure 1. Since the aluminas used were the same as in the previous study (Chantong and Massoth, 1983), the tortuosity at $\lambda = 0$ was taken to be 1.3 as found before. The logarithms of the group parameter $D_e/D_b\epsilon$ decrease approximately linearly with increasing λ at each temperature. The slopes determined from least-squares analyses are 5.7 ± 1.1 at 298 K, 4.6 ± 0.9 at 313 K, and 3.6 ± 1.0 at 333 K. The relative standard deviation of duplicate runs was 22%. Since the error in the slopes are close to the experimental error of repeat runs, the correlation of Eq. 2 is reasonable. Thus, the slopes decrease with increasing temperature, indicating that the restrictive effect becomes less prominent as temperature increases. Hence, pore restriction is not only a function of λ, but also of temperature.

Steric hindrance at the entrance to the pores and frictional resistance (hydrodynamic drag) within the pores are thought to be possible causes of restriction for diffusion (Renkin, 1954). The first factor expresses the condition that for entrance into a pore, a molecule must pass through the opening without striking the edge. The second factor denotes the friction between a molecule moving within a pore and its walls. The energy barrier in pore diffusion depends on the hydrodynamic drag. As the diffusing molecule has a larger kinetic energy at elevated temperature, it becomes easier to pass the energy barrier.

The effect of temperature on the restrictive factor can be empirically expressed by a temperature-dependent restrictive factor, α, *viz.*,

$$F(\lambda) = e^{-\alpha\lambda} \qquad (3)$$

where α is given by the slopes in Figure 1. An Arrhenius plot of α vs. $1/T$ for the data at hand gave a temperature response of 10.9 ± 4.2 kJ/mol. The equation relating the restrictive coefficient with temperature is,

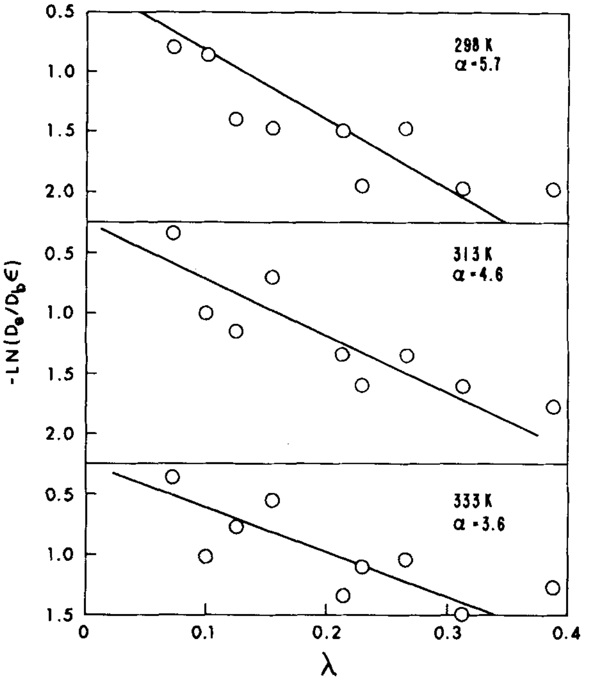

Figure 1. Variation of $D_b/D_e\epsilon$ with λ.

$$ln\,\alpha = 1.30/T - 2.62 \qquad (4)$$

Using this relationship and Eq. 3 it is possible to estimate the temperature above which restriction in diffusion can be neglected ($F(\lambda) > 0.9$). For example, at a temperature of 625 K, a typical reaction temperature for hydrodesulfurization (Gates et al., 1979), a restrictive factor of 0.89 is predicted for $\lambda = 0.2$ and a value of 0.75 for $\lambda = 0.5$. Hence, restrictive diffusion may be important under hydroprocessing conditions when the molecular size of the reactants are sufficiently large compared to the catalyst pore size. Since the true effective diffusivity will be decreased by the restrictive factor, the restrictive factor would contribute to an additional lowering of the effectiveness factor of the catalyst calculated by conventional methods (Satterfield and Sherwood, 1963). However, it should be cautioned that the restrictive factors were obtained over a limited temperature range and extrapolation to higher temperatures is uncertain.

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NOTATION

D_b = bulk diffusivity
D_e = effective diffusivity
$F(\lambda)$ = restrictive factor
T = temperature

Greek Letters

α = restrictive coefficient
ϵ = porosity
λ = ratio of molecular diameter of solute to pore diameter of alumina
τ = tortuosity
τ_o = tortuosity at $\lambda = 0$

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Thermal Regeneration of the Phenol-Carbon System

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Suzuki et al. (1978) divided the characteristics of thermal regeneration of spent activated carbon into three types according to the kind of adsorbate. Phenol, and other aromatic compounds with side chains, constituted type III adsorbates that were found to be desorbed slowly on heating and to leave a large residue at 1,073 K. We have confirmed this behavior with thermal gravimetric measurements (TGA experiments) for phenol adsorbed on a bituminous-base, activated carbon (Type BPL from Pittsburgh Activated Carbon Co.). However, the main purpose of this note is to describe the data of thermal regeneration as a function of temperature.

ADSORPTION ISOTHERMS

Figure 1 shows equilibrium isotherms for three different adsorbates, sucrose (Chihara et al., 1981), sodium dodecylbenzene sulfonate (DBS) (Umehara et al., 1982), and phenol, at 298 K on type BPL carbon. This carbon, whose complete properties are available (Chihara et al., 1981), has a broad pore size distribution (5 to >10,000 × 10^{-10}m) and a high surface area (1 × 10^6 m^2/kg). The carbon (2.1 × 10^{-4} to 3.2 × 10^{-4} m particles) used for preparing the samples was first boiled with distilled water to remove fines and dried at 393 K in an oven until there was no further weight change. Then the particles were added to phenol-water solutions and placed in shakers in a bath at 298 K for three days. The upper isotherms for phenol were obtained from the phenol concentrations [determined by spectrophotometric (UV) analysis] of the solutions before and after adding the carbon particles. The lower isotherms were obtained by filtering the particles, drying in an oven at 393 K to constant weight (about three days), and weighing.

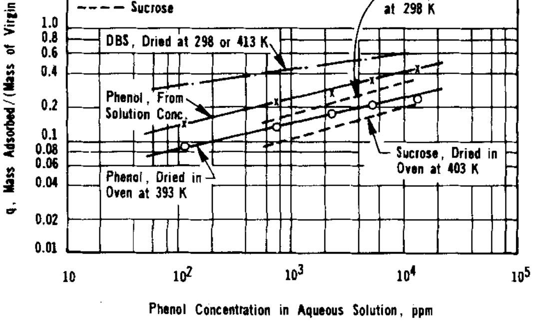

Figure 1. Adsorption isotherms: phenol on BPL carbon at 298 K.

Over the concentration ranges shown, all the isotherms are of the Freundlich type (straight lines in Figure 1). The adsorption capacity for phenol is somewhat higher than that for sucrose. The two isotherms for these two adsorbates indicate that about 38% of the adsorbed material is removed by drying in air at 393–403 K. In the case of sucrose, the desorbed material must be volatile decomposition products, while for phenol either volatile decomposition products or phenol itself could be evaporating from the carbon. Seewald (1974) found that phenol on carbon can react at room temperature in the presence of air to produce volatile products and dibenzofuran and oxydiphenyl ether.

In contrast, the isotherm for DBS is the same for samples dried at either 298 or 413 K, indicating that there is no low-temperature decomposition. The adsorption capacity of the carbon for the DBS is significantly higher than that for either phenol or sucrose.

TGA DATA

A Perkin-Elmer TGA apparatus, modified but slightly from that employed by Chihara et al. (1981), was used to measure both the