

## Diffusion of Cyclohexanes in ZSM-5 Zeolites

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Diffusion coefficients have been measured for the diffusion of cyclohexane and alkylcyclohexanes ranging from methyl- to pentylcyclohexane in ZSM-5-type zeolites using the samples of flat plate-like crystallite. The uptake curves of cyclohexanes by these samples are considered to represent primarily the diffusion of cyclohexanes into the straight channel. The diffusion coefficient of cyclohexane at 377 K was  $4.8 \times 10^{-13}$  cm<sup>2</sup>/sec and they were  $9.9 \times 10^{-13}$ ,  $2.3 \times 10^{-13}$ ,  $2.6 \times 10^{-13}$ ,  $3.8 \times 10^{-13}$ , and  $5.4 \times 10^{-13}$  cm<sup>2</sup>/sec for methyl-, ethyl-, *n*-propyl-, *n*-butyl-, and *n*-pentylcyclohexane, respectively. The diffusion coefficients of monosubstituted *n*-alkylcyclohexane showed a minimum at ethylcyclohexane and increased steadily as the chain length got longer. The length of the ethylcyclohexane molecule is comparable to the intersection space and the sharp decrease in the diffusion coefficient can be interpreted in terms of the cage effect. The diffusion coefficient of *t*-1,4-dimethylcyclohexane was two orders of magnitude larger than that of ethylcyclohexane although they have about the same molecular length and kinetic diameter. This may be attributed to the methyl-methyl interaction resulting in a favorable orientation for diffusion through the intersection space. © 1988 Academic Press, Inc.

### INTRODUCTION

Diffusional mass transport of hydrocarbon molecules in the intracrystalline space plays an essential role in molecular shape-selective catalysis of ZSM-5-type zeolites.

The framework of ZSM-5-type zeolites contains two types of intersecting channels. The straight channels running parallel to the *y*-axis [010] of the orthorhombic unit cell have ca.  $5.4 \times 5.6$  Å free diameter (1). The sinusoidal channels along the *x*-axis [100] interconnected by the straight channels have somewhat smaller openings.

Olson *et al.* (2) studied the crystal structure and structure-related properties of ZSM-5-type zeolite. Ma and others studied the adsorption and diffusion of C<sub>6</sub> and C<sub>8</sub> hydrocarbons in silicalite (3) and modified HZSM-5 (4). Anderson *et al.* (5) compared the sorptive and catalytic properties of ZSM-5 zeolites with those of silicalite. Derouane and Gabelica (6) measured the adsorption capacities of several hydrocarbons on ZSM-5 and suggested that aromatics and methyl-substituted aliphatics have a

strong preference for the diffusion and adsorption in the straight channel.

For the experimental determination of diffusion coefficient by sorption technique, it is desirable to use the crystallites of uniform shape and size. The typical shape of ZSM-5 crystals is reported (7,8) to be a platelet shape with the (010) surface being the plate surface. The diffusion of cyclohexanes in ZSM-5 is slow and the external heat and mass transfer effect may be neglected. We have obtained ZSM-5 samples of rather uniform flat plate-like samples suitable for studying the diffusion of hydrocarbons primarily through the straight channels. Using these uniform flat plate-like samples of ZSM-5, diffusion coefficients have been measured for the diffusion of cyclohexane and alkyl-substituted cyclohexanes in ZSM-5.

### MATERIALS

For the synthesis of Al-free ZSM-5 samples, colloidal silica (29% SiO<sub>2</sub>, Snowtex, Nissan Chem.) was added to the aqueous solution of 10% tetrapropylammonium hy-

droxide (TPAOH, Tokyo Kasei) as organic base, as described in the literature (9). For Na-ZSM-5, sodium aluminate (35%  $\text{Al}_2\text{O}_3$ , Kanto Chem.) was dissolved in a demineralized water and added to silica sol containing TPAOH. Initial compositions of the sols for the samples were  $(\text{TPA})_2\text{O}-5\text{SiO}_2-700\text{H}_2\text{O}$  for p-1,  $(\text{TPA})_2\text{O}-20\text{SiO}_2-800\text{H}_2\text{O}$  for p-2, and  $14(\text{TPA})_2\text{O}-\text{NaAlO}_2-200\text{SiO}_2-10900\text{H}_2\text{O}$  for p-3. The sols were transferred to a stirred reactor (Parr Instrument, No. 4542) of 2000 ml and crystallized at autogenous pressure at 453–473 K for 2 days with vigorous stirring. After completion of the reaction, the reactor was cooled in atmosphere, and the products were filtered, dried overnight at 373 K, and calcined at 773 K for 15 hr. The crystallites were characterized by X-ray diffractometry, scanning electron microscopy, and  $\text{N}_2$  adsorption. The crystallites obtained had a flat plate-like shape and the thicknesses of samples p-1, p-2, and p-3 were 0.3, 0.5, and 0.8  $\mu\text{m}$ , respectively. The chemical analyses and pore volumes of the samples are listed in Table 1.

Cyclohexane (>99%), methyl- (>99%), ethyl- (>98%), propyl- (>98%), butyl- (>99%), pentyl- (>98%), and *t*-1,4-dimethylcyclohexane (>95%) used for the diffusion measurements were Tokyo Kasei's guaranteed reagents.

#### METHOD

Uptake curves of cyclohexane and alkylcyclohexanes were determined volumet-

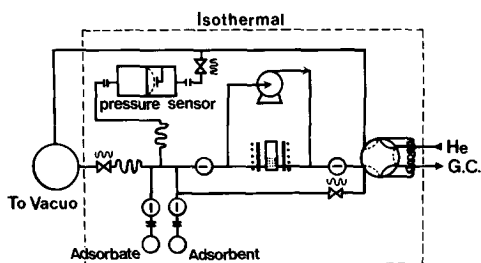


FIG. 1. Schematic diagram of volumetric adsorption system.

TABLE I  
Chemical Analysis and Pore Volumes  
of the ZSM-5 Samples

	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$ (wt%)	$\text{Na}_2\text{O}$	Pore volume <sup>a</sup> ( $\text{cm}^3/\text{g}$ )
p-1	99.5	0.2	—	0.189
p-2	99.8	0.3	—	0.186
p-3	98.8	0.8	0.03	0.182

<sup>a</sup> Pore volume was taken as the amount of nitrogen adsorbed at liquid nitrogen temperature and at  $P/P_0 = 1$ , assuming that the adsorbate within the channels has the normal liquid density.

rically. The pressure was monitored by a Datametrix capacitance manometer system (Model 5310, 1173). A schematic diagram of the adsorption unit is shown in Fig. 1. The temperature of the whole unit was controlled within  $\pm 1$  K. Before each run, the sample was activated under vacuum at 623 K. The diffusion equation in a plane-sheet was applied to obtain the diffusion coefficients. When the surface concentration of the diffusing molecules is uniform and the diffusion coefficient is constant, one-dimensional diffusion in a plane-sheet of thickness  $2L$  ( $l_0$ ) may be expressed as

$$\frac{Q_t}{Q_\infty} = 2 \left( \frac{Dt}{L^2} \right)^{1/2} \left\{ \pi^{-1/2} + 2 \sum_{n=1}^{\infty} (-1)^n \operatorname{ierfc} \frac{nL}{\sqrt{Dt}} \right\}, \quad (1)$$

where  $Q_\infty$  is the amount taken up at infinite time and  $Q_t$  is that at time  $t$ .

#### RESULTS

The scanning electron micrographs of the three samples of synthesized ZSM-5-type crystals used for the diffusion measurements are shown in Fig. 2. The shape of the crystallites is one of a flat plate-like structure and the thicknesses (the length along the *b*-axis) of the crystallites are 0.3, 0.5, and 0.8  $\mu\text{m}$ , respectively. Figures 3a–3g show the uptake curves for (a) cyclohexane, (b) methylcyclohexane, (c) ethylcyclo-

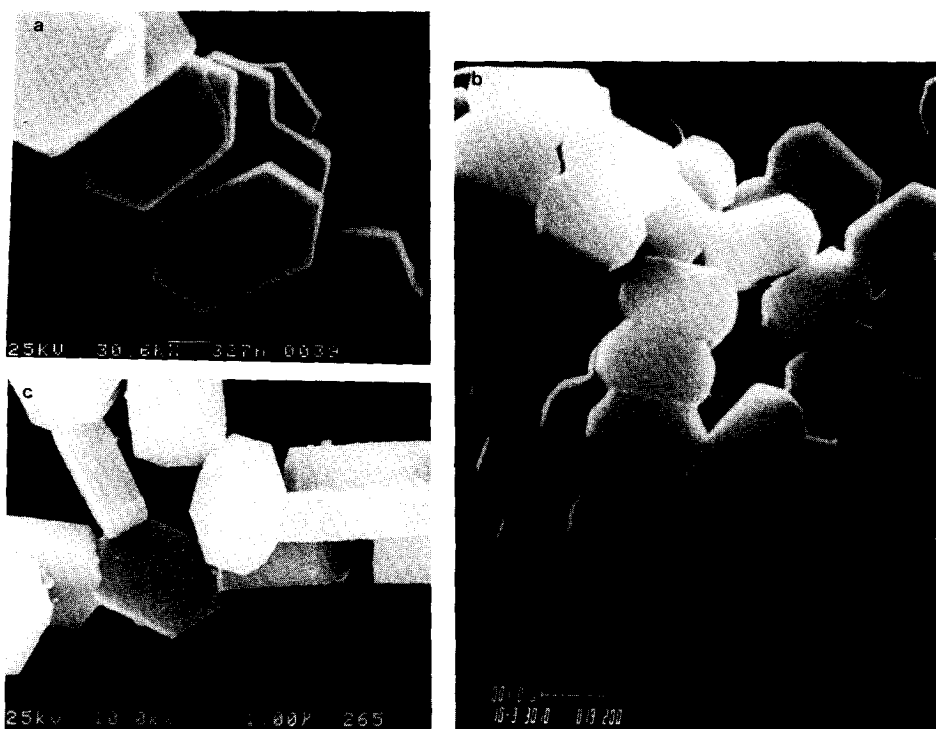


FIG. 2. Scanning electron micrographs of ZSM-5 zeolite samples. (a) p-1; (b) p-2; (c) p-3.

hexane, (d) *n*-propylcyclohexane, (e) *n*-butylcyclohexane, (f) *sec*-butylcyclohexane, and (g) *t*-1,4-dimethylcyclohexane at varying temperature. In Fig. 4, the uptake curves for the above-mentioned cyclohexanes at 377 K are compared. Figure 5 illustrates the temperature dependence of diffusivity of cyclohexanes in ZSM-5 zeolite. Table 2 summarizes the results of diffusion coefficients and activation energies for diffusion. In Table 3, the diffusion coefficients and adsorption capacities of cyclohexanes in ZSM-5 zeolite at 377 K are compared. Diffusion coefficients at 377 K decreased in the order  $D(t\text{-}1,4\text{-dimethylcyclohexane}) > D(\text{methylcyclohexane}) > D(n\text{-pentylcyclohexane}) > D(\text{cyclohexane}) > D(n\text{-butylcyclohexane}) > D(n\text{-propylcyclohexane}) > D(\text{ethylcyclohexane}) > D(\text{sec-butylcyclohexane})$  as shown in Table 2 and Fig. 4. The diffusion coefficient of *t*-1,4-dimethylcyclohexane is two orders of magnitude larger than that of ethylcyclohexane despite the

fact that both molecules have the same molecular length. The diffusion coefficients of *n*-propylcyclohexane, *n*-butylcyclohexane, and *n*-pentylcyclohexane are larger than that of ethylcyclohexane. The latter with a shorter molecular length was expected to have a larger diffusion coefficient than *n*-propylcyclohexane, *n*-butylcyclohexane, and *n*-pentylcyclohexane. The activation energies for diffusion were calculated using the Arrhenius relationship  $D = D_0 \exp(-E/RT)$ . Activation energies for diffusion obtained between the temperatures of 330–390 K for *n*-alkylcyclohexane increase steadily as the chain lengths get longer. For *t*-1,4-dimethylcyclohexane, the activation energy is 5.7 kcal/mole considerably lower than that of ethylcyclohexane. The adsorption capacity at 377 K is four molecules per unit cell for cyclohexane. Adsorption capacity decreases as the chain length of the alkyl group increases and it is 3.7 molecules for *n*-butylcyclohexane. To see the effect of

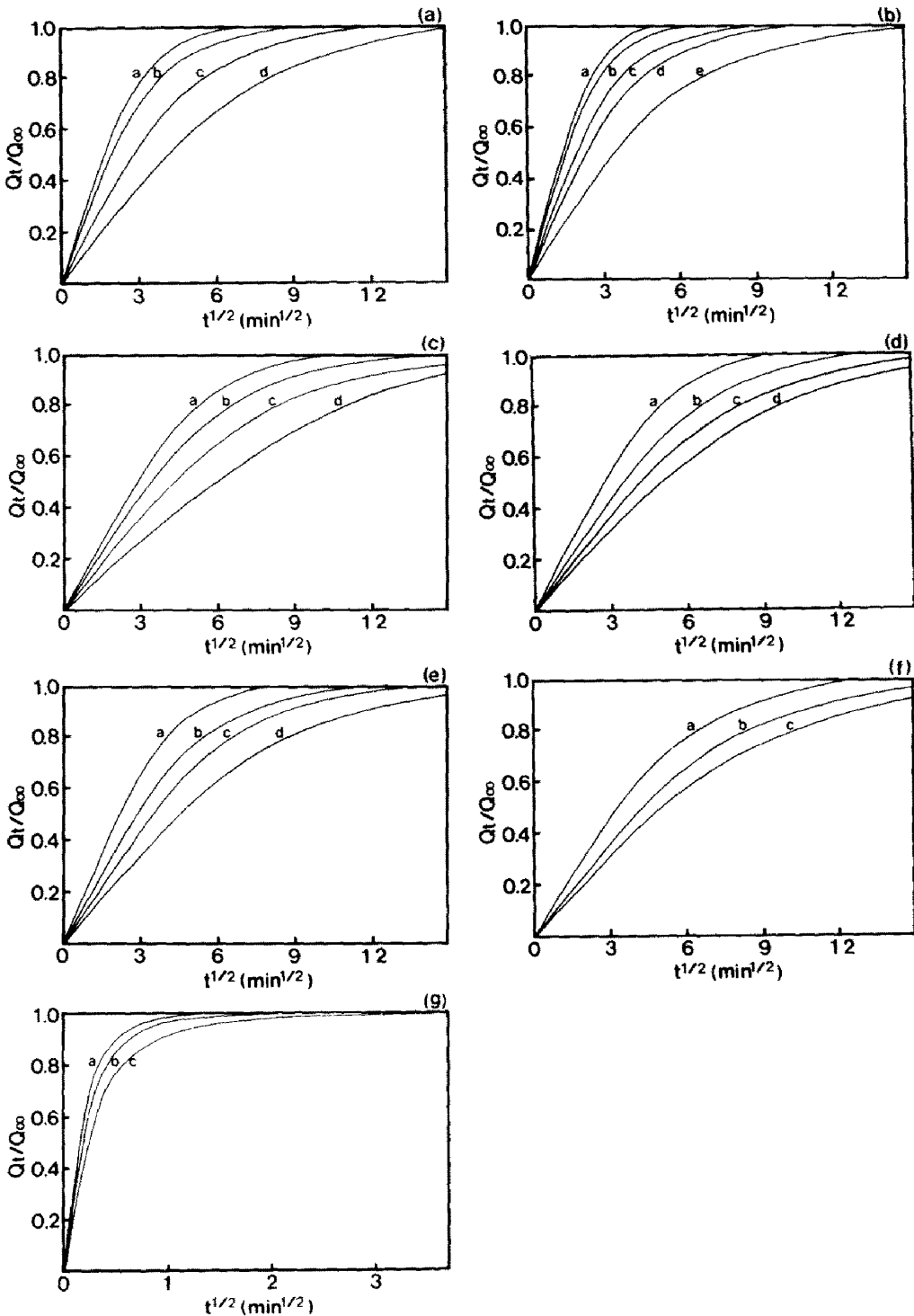


FIG. 3. Sorption kinetics of cyclohexanes in  $0.5 \mu\text{m}$  ZSM-5. (a) Cyclohexane: a, 388 K; b, 377 K; c, 364 K; d, 348 K. (b) Methylcyclohexane: a, 377 K; b, 372 K; c, 361 K; d, 351 K; e, 399 K. (c) Ethylcyclohexane: a, 377 K; b, 371 K; c, 362 K; d, 351 K. (d) *n*-Propylcyclohexane: a, 377 K; b, 369 K; c, 361 K; d, 355 K. (e) *n*-Butylcyclohexane: a, 377 K; b, 368 K; c, 361 K; d, 356 K. (f) *sec*-Butylcyclohexane: a, 381 K; b, 374 K; c, 369 K. (g) *t*-1,4-Dimethylcyclohexane: a, 377 K; b, 368 K; c, 351 K.

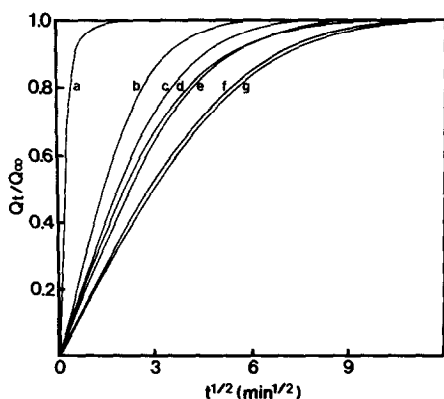


FIG. 4. Sorption kinetics of cyclohexanes in  $0.5 \mu\text{m}$  ZSM-5 at 377 K. (a) *t*-1,4-Dimethylcyclohexane; (b) methylcyclohexane; (c) *n*-propylcyclohexane; (d) cyclohexane; (e) *n*-butylcyclohexane; (f) *n*-propylcyclohexane; and (g) ethylcyclohexane.

TABLE 2

Diffusion Coefficients and Activation Energies for Diffusion of Cyclohexanes in ZSM-5 Zeolites

Adsorbate	Temperature (K)	Diffusion coefficient ( $\text{cm}^2/\text{sec}$ )	$E$ (kcal/mole)
Cyclohexane	348	$1.2 \times 10^{-13}$	12.1
	364	$2.6 \times 10^{-13}$	
	377	$4.8 \times 10^{-13}$	
	388	$7.1 \times 10^{-13}$	
Methylcyclohexane	339	$1.7 \times 10^{-13}$	11.7
	351	$3.5 \times 10^{-13}$	
	361	$5.2 \times 10^{-13}$	
	372	$8.3 \times 10^{-13}$	
	377	$9.9 \times 10^{-13}$	
Ethylcyclohexane	351	$6.4 \times 10^{-14}$	12.9
	362	$1.1 \times 10^{-13}$	
	371	$1.7 \times 10^{-13}$	
	377	$2.3 \times 10^{-13}$	
<i>n</i> -Propylcyclohexane	355	$8.6 \times 10^{-14}$	13.2
	361	$1.2 \times 10^{-13}$	
	369	$1.7 \times 10^{-13}$	
	377	$2.6 \times 10^{-13}$	
<i>n</i> -Butylcyclohexane	356	$1.1 \times 10^{-13}$	15.8
	361	$1.5 \times 10^{-13}$	
	368	$2.3 \times 10^{-13}$	
	377	$3.8 \times 10^{-13}$	
<i>sec</i> -Butylcyclohexane	369	$8.0 \times 10^{-14}$	20.0
	371	$9.5 \times 10^{-14}$	
	374	$1.2 \times 10^{-13}$	
	381	$1.9 \times 10^{-13}$	
<i>t</i> -1,4-Dimethylcyclohexane	351	$4.2 \times 10^{-11}$	5.7
	362	$5.6 \times 10^{-11}$	
	368	$6.1 \times 10^{-11}$	
	377	$7.4 \times 10^{-11}$	
<i>n</i> -Pentylcyclohexane	377	$5.4 \times 10^{-13}$	

TABLE 3

Adsorptive and Diffusive Properties of Cyclohexanes in ZSM-5 Zeolite at 377 K

Adsorbate	Molecular length ( $\text{\AA}$ )	Diffusion coefficient ( $\text{cm}^2/\text{sec}$ )	Adsorption capacity	
			(mg/g)	(molec./U.C.)
Cyclohexane	6.00 <sup>a</sup>	$4.8 \times 10^{-13}$	58.4	4.0
Methylcyclohexane	7.26	$9.9 \times 10^{-13}$	65.7	3.9
Ethylcyclohexane	8.52	$2.3 \times 10^{-13}$	72.9	3.8
<i>n</i> -Propylcyclohexane	9.78	$2.6 \times 10^{-13}$	82.3	3.8
<i>n</i> -Butylcyclohexane	11.04	$3.8 \times 10^{-13}$	88.8	3.7
<i>n</i> -Pentylcyclohexane	12.30	$5.4 \times 10^{-13}$	88.8	3.3
<i>t</i> -1,4-Dimethylcyclohexane	8.52	$7.4 \times 10^{-11}$	74.0	3.8

<sup>a</sup> See Ref. (13).

crystallite thickness, diffusion coefficients of cyclohexane were compared for the samples of differing thickness. Figure 6 shows the uptake curves for the samples of 0.3, 0.5, and  $0.8 \mu\text{m}$ . The value obtained was the same for all three samples giving  $7.1 \times 10^{-13} \text{ cm}^2/\text{sec}$  at 388 K.

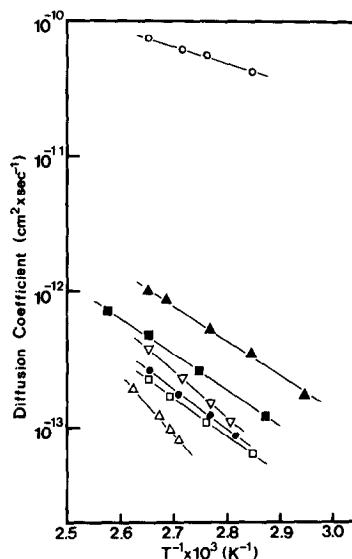


FIG. 5. Temperature dependence of diffusivity of cyclohexanes in ZSM-5.  $\circ$ , *t*-1,4-Dimethylcyclohexane;  $\blacktriangle$ , methylcyclohexane;  $\blacksquare$ , cyclohexane;  $\nabla$ , *n*-butylcyclohexane;  $\bullet$ , *n*-propylcyclohexane;  $\square$ , ethylcyclohexane; and  $\triangle$ , *sec*-butylcyclohexane.

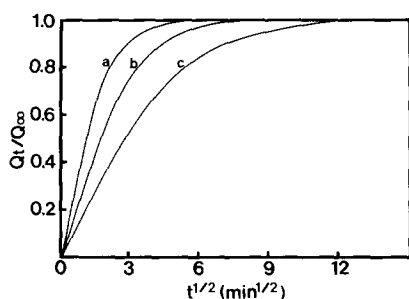


FIG. 6. Sorption kinetics of cyclohexane in (a) 0.3  $\mu\text{m}$  ZSM-5, (b) 0.5  $\mu\text{m}$  ZSM-5, and (c) 0.8  $\mu\text{m}$  ZSM-5 samples at 388 K.

### DISCUSSION

Scanning electron micrographs of the sample crystallites show typical ZSM-5 crystals of flat plate-like shape. The straight channels are perpendicular to the (010) surface and pass through it. The (010) surface makes up a major portion of the total surface of the crystallites and the diffusion may be approximated as one-dimensional diffusion through the straight channels of length  $L$  where  $2L$  is the thickness of the crystallites. The pore diameter of the sinusoidal channel is somewhat smaller than that of the straight channel and it would be more difficult for the cyclohexanes to diffuse into the sinusoidal channel than into the straight channel. It therefore seems reasonable to assume that the uptake curves represent primarily the diffusion of cyclohexanes into the straight channel. The results that the same diffusion coefficient was obtained from the measurements using the crystallites of differing thickness support our assumption.

The activation energy for diffusion increased with increasing chain length for monosubstituted  $n$ -alkylcyclohexanes. This may be attributed to the increased interaction with the internal surface with increasing chain length.

The diffusion coefficient of alkylcyclohexanes was expected to decrease with the increasing length of the alkyl group due to the interaction of the alkyl group with the

internal surface. The fact that the diffusivity of ethylcyclohexane decreased sharply from that of methylcyclohexane and was the lowest among methyl-, ethyl-, propyl-, butyl-, and pentylcyclohexane can be interpreted in terms of the cage (or window) effect. Goring (11) observed a minimum in diffusivity at  $n\text{C}_8$  for the diffusion of normal paraffins in zeolite T rising rapidly to a maximum at about  $n\text{C}_{12}$ . From cracking long-chain normal paraffins over erionite, Chen *et al.* (12) observed a cage effect on product distribution in that almost no product appeared in the  $\text{C}_8$  range. The length of the ethylcyclohexane molecule is comparable to the intersection space and this leads to a sharp decrease in the diffusivity. For a molecule longer than ethylcyclohexane molecule, one end of the molecule extends into the next unit providing a more favorable configuration for transit through the intersection. A steady increase in the diffusivity from propylcyclohexane to pentylcyclohexane may be the result of an increased orientational effect of the longer chain. The fact that the diffusivity of  $t$ -1,4-dimethylcyclohexane is two orders of magnitude larger than that of ethylcyclohexane is rather striking since both molecules have about the same molecular length and kinetic diameter. The enhanced diffusivity of  $t$ -1,4-dimethylcyclohexane may be attributed to the methyl-methyl interaction resulting in a quite favorable orientation for diffusion through the intersection space.

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