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Transient Diffusion in Solids with a Bipore Distribution

Transient diffusion of *n*-butane, iso-butane, and 1-butene in synthetic CaX(Na) spherical pellets is studied in a constant volume, well-stirred system. The intracrystalline diffusion coefficients are in the order of 10^{-14} cm^2/s, and the activation energy is about 7.0 Kcal/g-mole. Experimental data agree well with a mathematical model developed to describe transient diffusion.

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SCOPE

The diffusion in porous pellets formed from zeolite crystals usually involves two main mechanisms: diffusion through the micropore structure within the crystals (intracrystalline diffusion) and diffusion through macropore structure between crystals (intercrystalline diffusion). The determination of each individual diffusion coefficient can be of importance in data interpretation and improving engineering design in operations such as purification, separation, and catalytic conversions.

Previous work on the study of diffusion in zeolites concentrated mostly in micropore diffusion with powder forms. Recent studies on the diffusion in solids with a bipore distribution include the theoretical and experimental investigation of diffusion in ion exchanged resins by Ruckenstein et al. (1971), the experimental study of diffusion of carbon dioxide in commercial 5A pellets by Sargent and Whitford (1971), and mathematical and experimental investigation of diffusion in Linde 13X by Ma and Ho (1974). All the above-mentioned studies were performed under constant pressure conditions. The present work employed a constant volume technique to examine quantitatively the diffusion of C_4-hydrocarbons in micropores. Diffusion coefficients were evaluated based on a mathematical model taking into account intercrystalline and intracrystalline diffusion and adsorption under constant volume conditions. Rates of sorption of *n*-butane, iso-butane, and 1-butene in synthetic CaX(Na) were measured at three temperatures, and the activation energies for diffusion were determined from an Arrhenius plot.

CONCLUSIONS AND SIGNIFICANCE

Micropore diffusion coefficients were determined by assuming that the transport processes in macropores and micropores obey Fick's equation. The activation energy for diffusion was found to be about 6 to 8 Kcal/g-mole for the C_4-hydrocarbons used in the study. The relatively low activation energy may, in part, be due to the large openings of the zeolite X.

A mathematical model was developed to describe the diffusion in a solid with a bipore distribution. The present model differs from previous studies in that it deals with a well-stirred system where the total quantity of the diffusing species is finite. Agreement between experimental data and theoretical results was good. It should be noted that the present model can be reduced to those developed

by previous investigators. Moreover, the model can be applied to measure the diffusion coefficients in a multicomponent sorbate system if the diffusion coefficients are assumed to be constant.

The significance of using such a model to treat the experimental data obtained from diffusion measurements on zeolite pellets under constant volume conditions was demonstrated by the fact that the calculated intracrystalline diffusion coefficient based on a simple Fick's equation would be two orders of magnitude smaller than that obtained from the present calculation.

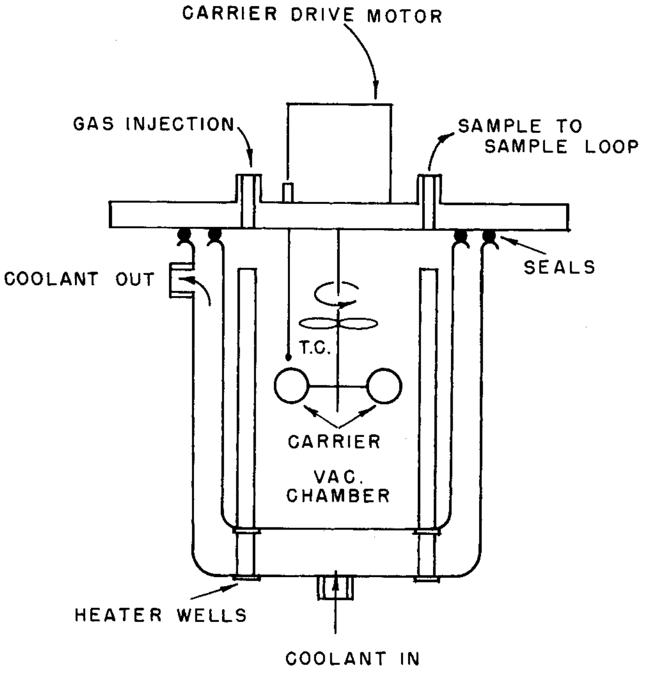

Fig. 1. Constant volume reactor.

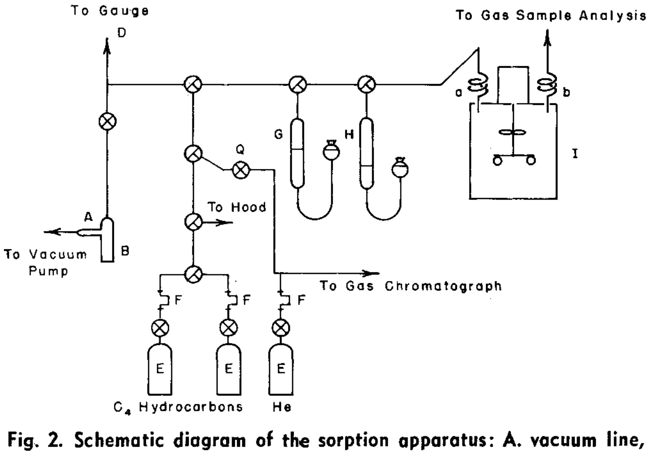

Fig. 2. Schematic diagram of the sorption apparatus: A. vacuum line, B. mercury trap, a. sorbate inlet, b. sample outlet, D. MacLeod vacuum gauge, E. gas cylinder, F. moisture trap, G. 300 cm^3 gas burette, H. 100 cm^3 gas burette, I. sorption reactor, Q. carrier gas valve.

Measurements of diffusion coefficients and an understanding of transport mechanisms within a porous material are important in designing separation processes and catalytic conversion units. Volumetric and gravimetric methods are commonly employed for such studies. The latter is generally employed for the study of diffusion of a pure component into porous sorbents, and the mathematics involved are relatively simple. The former normally involves measurements of pressure change and can be applied to study the diffusion of a multicomponent system if gaseous compositions are measured as a function of time. However, the mathematics required for such a system are more complicated, especially if the sorbent possesses a bipore distribution (that is, commercial molecular sieve pellets). A single effective diffusion coefficient is sometimes used to interpret experimental results due to the lack of adequate mathematical solutions, but such an interpretation may lead to erroneous results (Furusawa and Smith, 1973; Ma and Ho, 1974).

Both theoretical and experimental work in the area of diffusion within solids with a bidisperse structure has recently been reported by Ruckenstein et al. (1971) and Sargent and Whitford (1971), as briefly summarized by Ma and Ho (1974). Ma and Ho (1974) developed a model which takes into account the diffusion in both macropores and micropores. They applied their model to determine intercrystalline and intracrystalline diffusion coefficients of allene and methylacetylene in synthetic faujasite pellets in the temperature range between 21° and 60°C. Good agreement between experimental and theoretical results were reported by them.

The present study is concerned with the diffusion of *n*-butane, isobutane, and 1-butene in Davison CaX(Na) sieve in the temperature range between 5° and 60°C. Diffusion measurements were made on CaX(Na) beads formed from zeolite powder with 20% kaolite as the binder. The primary objective is to investigate the diffusion mechanisms of branched and straight chain saturated and unsaturated hydrocarbons. A mathematical model, which is applicable to transient diffusion from a well-stirred reservoir to solids having macropores as well as micropores, has been developed and applied to the determination of the intracrystalline diffusion coefficients. The interaction between the diffusing molecules and the ionic structure of the zeolite was also discussed.

APPARATUS AND PROCEDURE

A well-stirred constant volume sorption chamber consisting of a cylindrical stainless steel vessel of 3 l capacity was employed to study the sorption kinetics and sorption equilibrium. The agitator shaft was driven by a 1/12 hp motor at a constant speed of 3 300 rev/min. The spherical sorbent pellets (about 1 g of sorbent was normally used) were placed in two equally spaced adjustable baskets which were attached to the rotating shaft. The vessel is a modification of that used by Ma and Roux (1973) and is shown in Figure 1. Activation of the sorbent was done by three heating rods which were placed inside stainless steel casings (1.5 cm in diameter) to avoid the possible sorption of sorbate gas by the heating elements. The stainless steel casings were also used as baffles to facilitate mixing. The vessel is equipped with a cooling jacket for low temperature runs. The temperature of the system was controlled by a West controller to within ±0.5°C. A schematic diagram of the sorption system is shown in Figure 2.

Regeneration was done under a vacuum of about 5 μmHg at a temperature of 250°C for 10 hr. The same sample was used no more than five times, and no polymerization of 1-butane was observed after repeated outgas under vacuum at this temperature. After the adsorbent had been regenerated, the chamber was filled with helium and kept at atmospheric pressure by adjusting the mercury leveling bulb. The system temperature was controlled at a desired value. A measured amount of sorbate gas was then injected into the reactor through an injection port.

The gas phase concentration was measured by withdrawing the sample through the sampling loop and analyzed by a gas chromatograph. Ten to fifteen samples were taken, and the system was left running for about 4 hr. to obtain the equilibrium value which agrees with independent equilibrium measurements (Lee, 1976). The equilibrium loading ranges from 1.2 to 2.2 mmole/g-sorbent depending on temperature and sorbate gas used.

Helium and C_4 gases were research grade. Zeolite X was provided by Davison. Ion exchange of the NaX was done by contacting the zeolite with calcium acetate solution at room temperature. X-ray fluorescence analysis was employed to determine the amount of exchanged cation to be about 85% completion. X-ray diffraction analysis showed no change in crystal structure after the ion exchange. Twenty weight percent Georgia kaolin clay was added as a binder for the formation of spherical particles. It has been shown that the effect of the inert binder upon diffusion is negligible (Tamboli, 1970). The average radius of the particles is 0.230 cm, and the average crystal size as measured by an electron microscope is 1.08×10^{-4} cm.

RESULTS AND DISCUSSION

Mathematical Model

In the derivation of the mathematical model for zeolite particles, the assumptions made by Ma and Ho (1974) are also employed here. They are:

1. A spherical macroporous sorbent particle is an assembly of small microporous crystals which may be treated as homogeneous solids.
2. The crystals are spheres with a uniform size.
3. Diffusion in both the micropores and the macropores can be described by Fick's equation, and the diffusion coefficients are constant.
4. The adsorption isotherm is linear, and adsorption equilibrium is attained at the boundary surface of the crystals.

Now, consider N spherical particles immersed in a reservoir of well stirred fluid of volume V. Mass balances in both macropores and micropores give

$$\frac{D_a \epsilon_a}{\gamma_a^2} \frac{\partial}{\partial \gamma}\left(\gamma_a^2 \frac{\partial C_a}{\partial \gamma_a}\right) - \frac{3(1-\epsilon_a)}{R_i} D_i \left(\frac{\partial C_i}{\partial \gamma_i}\right)_{\gamma_i = R_i} = \frac{\partial C_a}{\partial t} \epsilon_a \tag{1}$$

$$D_i \left(\frac{\partial^2 C_i}{\partial \gamma_i^2} + \frac{2}{\gamma_i} \frac{\partial C_i}{\partial \gamma_i}\right) = \frac{\partial C_i}{\partial t} \tag{2}$$

Material balance in the fluid gives

$$V \frac{dC}{dt} = - N \epsilon_a D_a 4\pi R_a^2 \left(\frac{\partial C_a}{\partial \gamma_a}\right) \tag{3}$$

Equations (1), (2), and (3) should be solved with the following initial and boundary conditions:

$$C_a(o, \gamma_a) = C_a^o \tag{4a}$$

$$C_a(t, R_a) = C(t) \tag{4b}$$

$$C(o) = C^o \tag{4c}$$

$$C_i(t, R_i, \gamma_a) = K C_a(t, \gamma_a) \tag{4d}$$

$$C_i(o, \gamma_i, \gamma_a) = C_i^o \tag{4e}$$

$$\frac{\partial C_a(t, o)}{\partial \gamma_a} = \frac{\partial C_i(t, o, \gamma_a)}{\partial \gamma_i} = 0 \tag{4f}$$

The present system differs from previous studies in that it involves a time varying boundary condition [Equation (3)] due to the fact that the total quantity of diffusing species is finite. Thus, it is rather difficult to solve this set of equations. However, it is possible to solve this problem by employing techniques developed for numerical inversion of Laplace transforms. It should be emphasized that equilibrium is assumed to exist between the gas phase in the macropores and the surface of the zeolite crystals as shown by Equation (4*d*).

If one defines the following Laplace transform functions

$$\tilde{y}_a = \int_o^\infty y_a e^{-st} dt, \quad \tilde{y}_i = \int_o^\infty y_i e^{-st} dt \tag{5}$$

solution of Equations (1), (2), and (3) with boundary conditions (4) by the Laplace transform technique in terms of the normalized variables and parameters gives (Lee, 1976)

$$\tilde{y}(\eta_a, S) = \frac{\text{Sinh}\left[\eta_a \left\{S + \beta K \left(\sqrt{\frac{S}{\alpha}} \coth \sqrt{\frac{S}{\alpha}} - 1\right)\right\}^{1/2}\right]}{V_g \left[S + \beta K \left(\sqrt{\frac{S}{\alpha}} \coth \sqrt{\frac{S}{\alpha}} - 1\right)\right]^{1/2} \cosh \left[S + \beta K \left(\sqrt{\frac{S}{\alpha}} \coth \sqrt{\frac{S}{\alpha}} - 1\right)\right]^{1/2} + (S - V_g) \,\text{Sinh}\left[S + \beta K \left(\sqrt{\frac{S}{\alpha}} \coth \sqrt{\frac{S}{\alpha}} - 1\right)\right]^{1/2}} \tag{6}$$

Inversion of Equation (6) would normally require locating its singularities and application of inversion theorem. However, owing to the complexity involved in the inversion of Equation (6), a numerical scheme developed by Bellman (1964) was used to obtain the inversion of Equation (6). $y_a(\eta_a, t)$ can thus be evaluated. Once $y_a(\eta_a, t)$ is obtained, it is possible to obtain

$$\frac{C(t)}{C^o} = y_a(\eta_a = 1, t) \tag{7}$$

which is the change of sorbate concentration in the bulk phase and can be measured experimentally.

It should be noted that as V_g approaches zero, Equation (6) reduces to the form previously developed by Ma and Ho (1974). The numerical solution also approaches the solution of a simple unsteady state diffusion in a well-stirred fluid (Crank, 1957) for large α or small K. This is due to the fact that for large α the process is controlled by macropore diffusion, and as K approaches zero, only one type of pore exists. Thus, for both cases, the problem reduces to that of a simple unsteady state diffusion equation.

In addition to the fact that the present model can be reduced to the forms developed by the previous investigators, it should be noted that it can be expanded to the determination of mixture diffusion coefficients in a multicomponent sorbate system (Lee, 1976).

Some of the results calculated from Equations (6) and (7) are shown in Figures 3, 4, 5, and 6. It should be noted that in these figures the ratio of the sorbate concentration in the fluid phase at time τ and that at time infinity is plot-

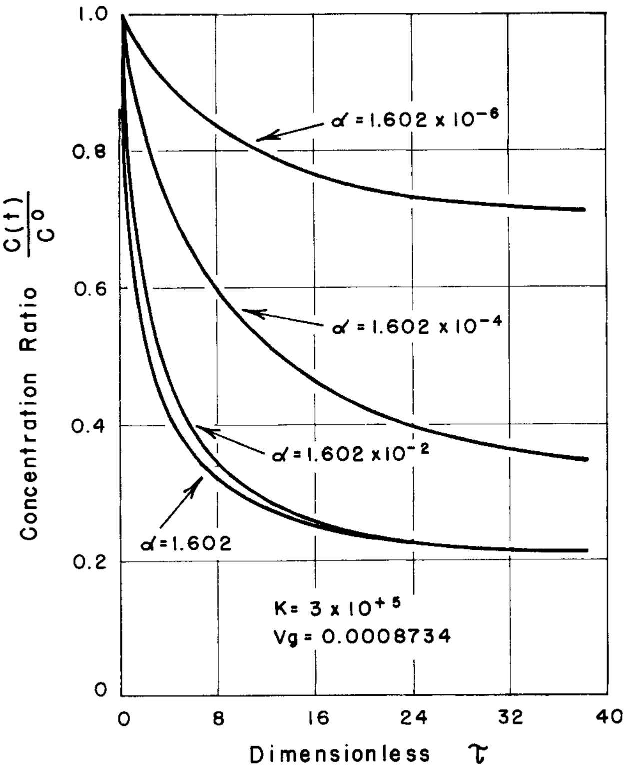

Fig. 3. Effect of dimensionless diffusivity ratio (α) on dimensionless concentration.

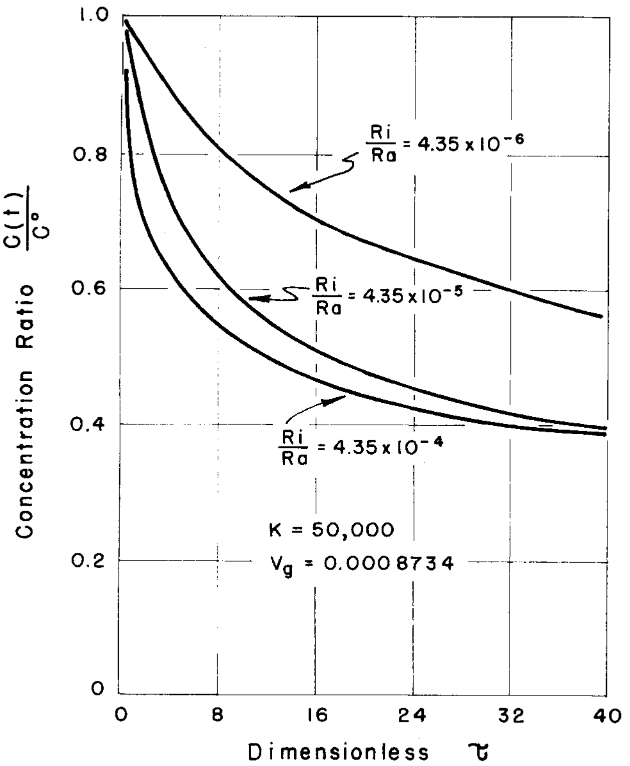

Fig. 5. Effect of crystal size on dimensionless concentration.

ted against dimensionless time instead of the conventional way of plotting M_t/M_∞ vs. square root of dimensionless time. It is felt that in a well-stirred system $C(t)$, the sorbate concentration in the fluid phase is a quantity which can be measured directly from experiments. Thus, these results can be conveniently applied to the evaluation of the diffusion coefficient.

Figures 3 and 4 show $C(t)/C^0$ as a function of dimensionless time with α as a parameter at a constant value of K

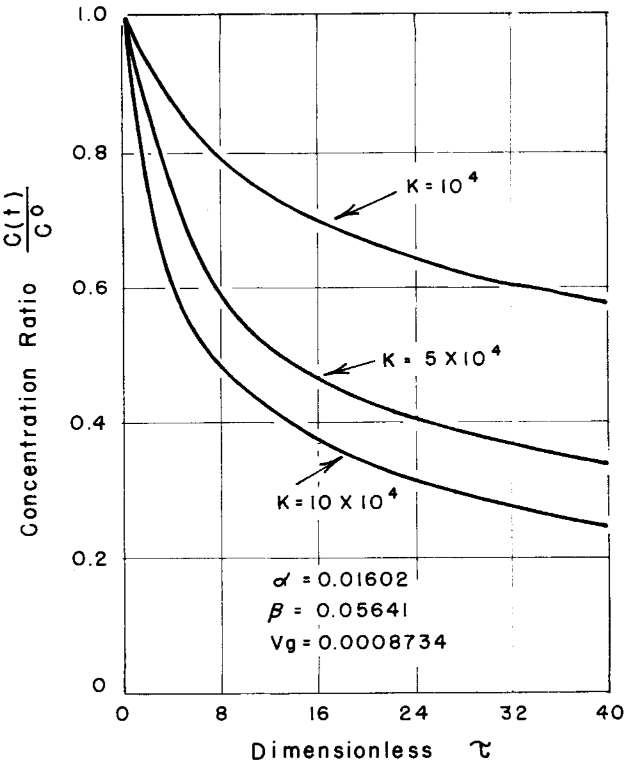

Fig. 4. Effect of equilibrium constant K on dimensionless concentration.

and with K as a parameter at a constant value of α, respectively. For large values of α or small values of K, the shape of the curve approaches that of a simple unsteady state diffusion as discussed previously (Ma and Ho, 1974; Ruckenstein et al. 1971). For $K = 3 \times 10^5$ as shown in Figure 3, $\alpha = 1.602 \times 10^{-6}$ and $\alpha = 1.602$ are approximately the limiting values for micropore and macropore controlled diffusion, respectively. Figure 5 shows the effect of crystal size on $C(t)/C^0$. It can be seen that when crystal size is decreased, the process becomes macropore controlled owing to large values of the time constant D_i/R_i^2. Such effects have been borne out by experiments carried out by Garg and Ruthven (1974, 1975). Figure 6 shows the effect of macroporosity (ϵ_a) upon $C(t)/C^0$. Again, at low porosity, the process is controlled by macropore diffusion.

Determination of Micropore Diffusion Coefficient

The mathematical model was employed to calculate the intracrystalline diffusion of C_4-hydrocarbons in CaX(Na) spheres. Experimental data were fitted with theoretical curves by the least-squares scheme. It should be noted that only D_i was varied in fitting the experimental data with theoretical curves. All other parameters employed in the calculations were determined independently, and their values are tabulated in Table 1. A typical comparison between theoretical results and experimental data is shown in Figure 7 which shows extremely good agreement between theoretical and experimental values. This seems to confirm the validity of the model. The calculated intracrystalline diffusion coefficients are tabulated in Table 1 for three temperatures.

The macropore diffusion coefficient was estimated by the following expression:

$$\frac{1}{D_{\text{eff}}} = \frac{1}{D_{K,\text{eff}}} + \frac{1}{D_{12,\text{eff}}} \qquad (8)$$

A tortuosity factor of 4.5 reported by Ma and Ho (1974) on a similar material was used in the calculation. The

Table 1. Results

	n-butane			iso-butane			1-butene		
Temp. °C	5	35	60	5	35	60	5	35	60
Initial amount m moles	1.95	1.88	1.89	1.93	1.90	1.95	2.48	1.81	1.88
E_i Kcal/g-mole		7.7			8.3			6.8	
K	85 700	31 487	9 816	60 900	18 012	6 851	94 617	81 938	40 565
R_a cm		0.2302			0.2302			0.2302	
R_i cm		1.08×10^{-4}			1.08×10^{-4}			1.08×10^{-4}	
D_a cm²/s	0.0685	0.0737	0.0778	0.067	0.0723	0.0764	0.0682	0.0736	0.0778
D_K cm²/s	0.383	0.402	0.418	0.383	0.402	0.418	0.389	0.410	0.426
D_i cm²/s	7.648×10^{-15}	1.93×10^{-14}	8.435×10^{-14}	9.314×10^{-15}	6.286×10^{-14}	1.074×10^{-13}	3.882×10^{-15}	8.217×10^{-15}	3.098×10^{-14}
ϵ_a		0.5			0.5			0.5	
Tortuosity factor		4.5			4.5			4.5	

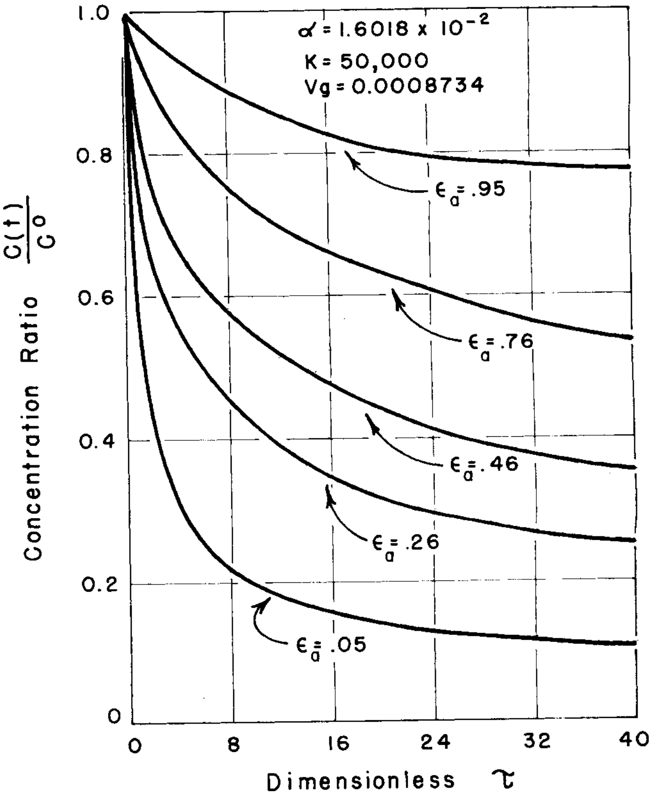

Fig. 6. Effect of macroporosity on dimensionless concentration.

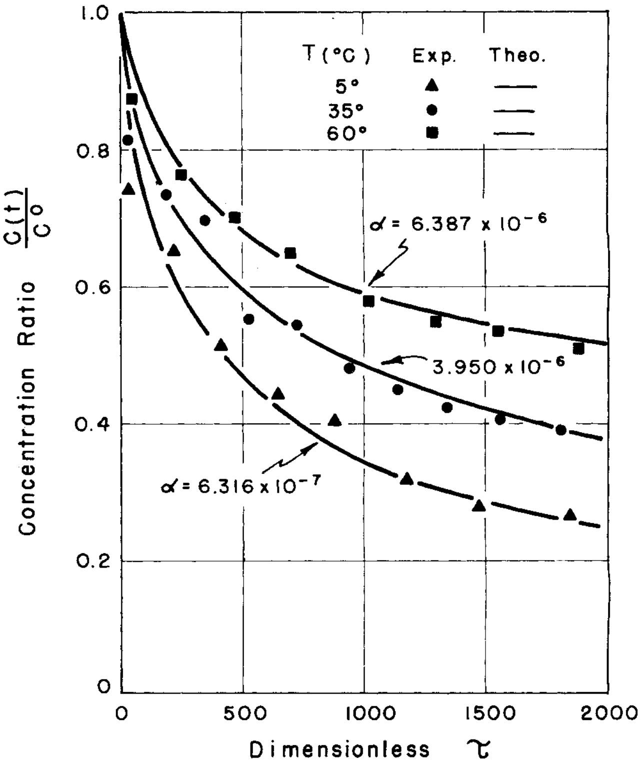

Fig. 7. Comparison of experimental and theoretical sorption curves for isobutane on CaX(Na) beads.

equilibrium constant K was determined from equilibrium adsorption measurements. The Arrhenius plot of the micropore diffusion coefficient as a function of temperature is shown in Figure 8. The activation energy calculated from the Arrhenius plot is listed in Table 1. The relatively low activation energy is, in part, due to the large opening of the zeolite X.

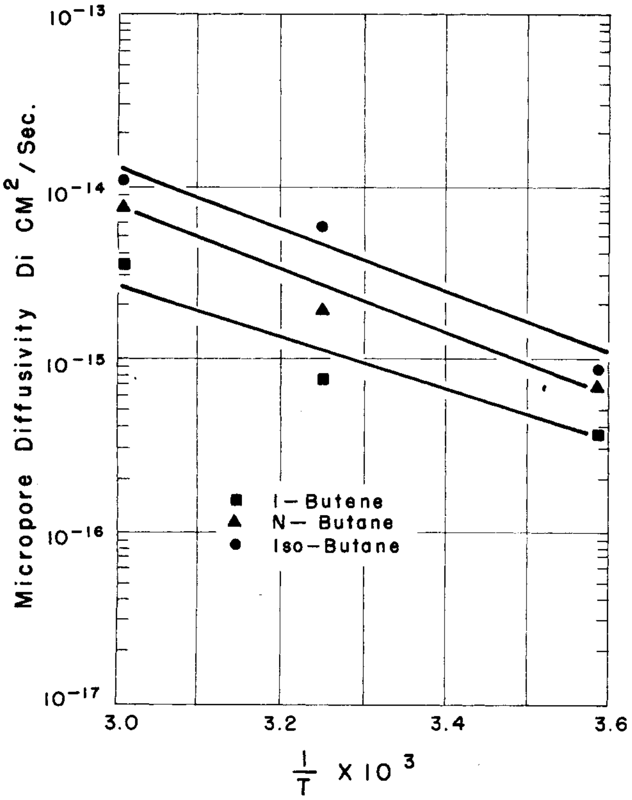

Fig. 8. Arrhenius plot of microprobe diffusivity as a function of temperature for CaX(Na) beads.

The micropore diffusion coefficient is in the range of 10^{-13} to 10^{-15} cm^2/s, which is somewhat lower than that previously reported by Ma and Ho (1974) and higher than that reported by Riekert (1971) on similar systems. The magnitude of the micropore diffusion coefficient is in the following order for the three gases: iso-butane > n-butane > 1-butene. As the pore openings are relatively larger than the molecular size of all three diffusing gases, it seems reasonable to compare their overall sizes. An estimate of the effective sizes of these three molecules by the bond length, bond angle, relative orientation of the atoms, and carbon-carbon bond rotation (Stevenson and Merril, 1975) indicates that isobutane is somewhat smaller than n-butane and 1-butene and thus can diffuse faster than the other two gases. In addition, the interaction between the cation and the diffusing molecules will be greater for 1-butene owing to the presence of the double bond (π bond). Strong interaction between the cation and the diffusing molecules would slow down the molecular movement and thus give low diffusion coefficient.

The significance of using such a bipore distribution model may be demonstrated by a simple calculation. One may wish to neglect the diffusion in macropores and use the solution of the simple unsteady state diffusion equation to calculate the intracrystalline diffusion coefficient. By using the present data, the intracrystalline diffusion coefficient calculated in this manner is approximately 10^{-16} cm^2/s, which is about two orders of magnitude smaller than the true value.

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NOTATION

C = concentration of sorbate, m moles cm^{-3}
D = diffusion coefficient, $cm^2\ s^{-1}$
D_K = Knudsen diffusion coefficient, $cm^2\ s^{-1}$
E = activation energy, Kcal $mole^{-1}$
K = equilibrium constant
N = number of adsorbent particles
R = radius, cm
r = radial distance, cm
t = time, s
T = temperature, °K
V = volume of reactor, cm^3
y = $\eta \dfrac{C}{C^o}$ = transformed variable

Greek Letters

τ = Dat/Ra^2 = dimensionless time
η = $\dfrac{r}{R}$ = dimensionless radial distance
θ = $\dfrac{C(t)}{C^o}$ = concentration ratio
α = $\dfrac{D_i/R_i^2}{D_a/R_a^2}$
β = $\dfrac{3(1-\epsilon_a)}{\epsilon_a}\alpha$
ϵ = void volume

Subscripts

i = micropore
a = macropore
g = sorbent to reactor volume ratio

Superscripts

0 = initial value

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