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Sorption and Diffusion of SF_6 in Silicalite Crystals

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Abstract. Kinetic and equilibrium data for sorption of SF_6 in silicalite have been determined by the ZLC method. The equilibrium constants and adsorption energy are comparable with the values reported previously for SF_6-NaX. Intracrystalline diffusion is relatively rapid with diffusivities of order 10^{-7}–10^{-8} $cm^2 \cdot s^{-1}$ at temperatures in the range 30–90°C. The implications for the use of SF_6 as a probe molecule for assessing the integrity of silicalite membranes are considered.

Keywords:

Since sulfur hexaflouride (SF_6) is a bulky molecule with molecular diameter (∼6 Å) almost equal to the diameter of the silicalite micropores it has been widely used as a probe molecule to test the integrity of silicalite membranes (Baertsch et al., 1996; Funke et al., 1997). The implicit assumption is that the permeation rate through the intracrystalline pores should be very low so that any substantial flux of SF_6 is indicative of extracrystalline permeation through cracks or defects. However, there appear to have been no detailed measurements of the sorption kinetics and equilibria for the SF_6-silicalite system so assumptions concerning the intracrystalline transport rate are speculative. In order to provide a proper basis for interpretation of SF_6 permeation measurements we have studied the sorption kinetics and equilibria in large well formed silicalite crystals by the ZLC (zero length column) method. The results of that study are reported here.

Experimental

Measurements were carried out by the standard ZLC method (Kärger and Ruthven, 1992) using a small sample (∼1 mg) of large silicalite crystals (equivalent radius $R \simeq 25\ \mu$m)—see Fig. 1. Helium was used as the carrier with an on-line quadrupole mass spectrometer as the detector.

In the long time region the ZLC response curve (for a set of uniform spherical particles) approaches an asymptote defined by:

$$\frac{c}{c_0} = \frac{2L}{L(L-1)+\beta_1^2} \exp\left[-\beta_1^2 Dt / R^2\right] \qquad (1)$$

where β_1 is the first root of the equation:

$$\beta \cot \beta + L - 1 = 0 \qquad (2)$$

and the parameter L is defined by:

$$L = \frac{1}{3} \cdot \frac{F}{KV} \cdot \frac{R^2}{D} \qquad (3)$$

A plot of $\ln(c/c_0)$ vs. t thus yields a linear asymptote from the slope and intercept of which the equilibrium parameter (KV) and the diffusional time constant (R^2/D) can be derived.

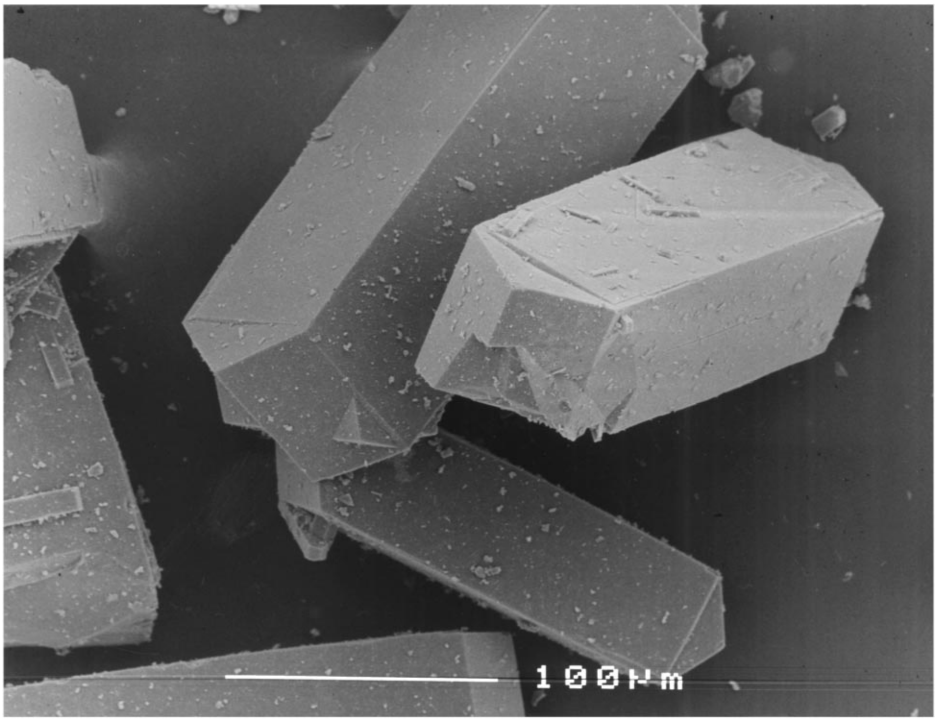

Figure 1. SEM photomicrograph of silicalite crystals.

The use of the diffusion equation in spherical from provides a convenient simplification. Even though the zeolite crystals are far from spherical this is a valid approximation since it has been shown that the effect of particle shape can be accounted for by use of a mean equivalent radius calculated as the radius of the sphere having the same external surface to volume ratio as the actual particles (see for example Kärger and Ruthven, 1992). Of course such an approach yields no information about non-isotropy and when applied to a non-isotropic material such as silicalite the resulting diffusivity is a weighted average of the diffusivities for the three principal directions.

Results and Discussion

Measurements were carried out at two different SF_6 concentration levels (1.8 and 3.5 Torr) in order to check the system linearity. A representative example of the response curves is shown in Fig. 2. The response is seen to be independent of the concentration level, confirming system linearity. A typical set of response curves (50°C, 1.8 Torr partial pressure) showing the effect of flow rate is presented in Fig. 3. The curves all have the form expected for a diffusion controlled system and the approach to the long time asymptote is clearly apparent.

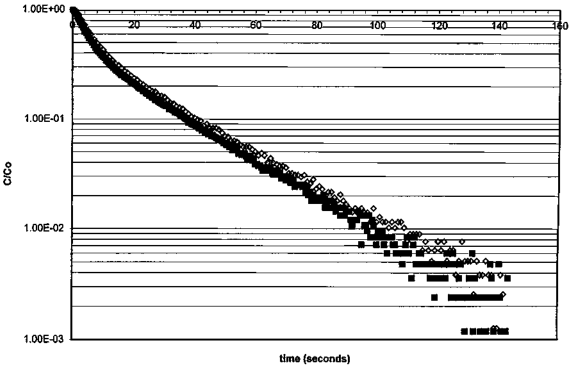

Figure 2. Experimental desorption curves for SF_6-silicalite at 50°C, 4.7 ml/min purge rate showing conformity between curves obtained at 1.8 Torr SF_6 (■) and 0.92 Torr SF_6 (◊).

The parameters extracted from the asymptotes of the experimental response curves are summarized in Table 1. The data at 50°C show very satisfactory consistency in that the values of D/R^2 and KV are almost

Table 1. Summary of experimental data for SF_6 silicalite.

T (K)	P (Torr)	F^a (ml/min)	Int	Slope (s^{-1})	L	$(D/r^2) \times 10^3$ (s^{-1})	KV (ml)	$D \times 10^8$ ($cm^2 \cdot s^{-1}$)
303	3.5	10	0.34	0.037	5.8	5.3	1.8	
	3.5	22	0.23	0.043	8.9	5.5	1.6	3.7
	3.5	42	0.15	0.055	12.8	6.5	2.7	
						Av 5.8	Av 2.4	
323	3.5	15	0.30	0.08	6.7	11	1.14	
	3.5	24	0.16	0.085	12.8	10	1.03	
	1.8	2.7	0.7	0.029	1.8	7.2	1.15	5.6
	1.8	4.7	0.45	0.042	4.0	7.0	0.93	
	1.8	11	0.30	0.063	6.9	8.6	1.05	
	1.8	23	0.14	0.081	14	9.6	0.97	
						Av 8.9	Av 1.04	
434	1.8	1.4	0.7	0.049	2.0	12	0.33	
		19	0.12	0.13	15	15	0.47	8.4
						Av 13.5	Av 0.40	
363	3.5	16	0.15	0.175	14	20	0.32	
	3.5	32	0.12	0.18	17	20.5	0.51	
	3.5	57	0.051	0.16	40	17	0.46	12.0
	1.8	9.5	0.15	0.152	14	18	0.21	
	1.8	23	0.10	0.197	21	20	0.30	
						Av 19.1	Av 0.36	

^{a}Corrected to column temperature.
$V \simeq 2.2 \times 10^{-3}$ ml.

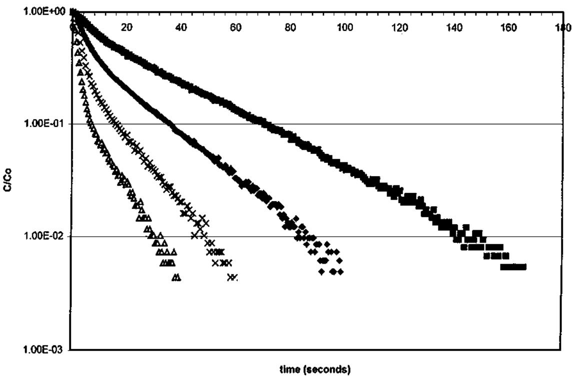

Figure 3. Experimental desorption curves for SF_6-silicalite at 50°C, 1.8 Torr showing effect of flow rate [2.7 ml/min (■); 4.7 ml/min (♦); 11 ml/min (×); 23 ml/min (△)].

constant regardless of flow rate or partial pressure. At other temperatures the values of KV are less consistent but values of D/R^2 are almost constant (at each temperature). Some variation in the values of KV is not unexpected since the intercept, and hence the L value from which KV is found, is much more sensitive than the slope to small deviations from linearity of the isotherm (Brandani, 1998).

Measurements with the same ZLC sample using a sorbate of known Henry constant (p-xylene) showed that the volume of the zeolite present in the column is approximately 2.2×10^{-3} ml. Using this value we may estimate dimensionless Henry constants from the product KV. Details are given in the thesis of MacDougall (1998). These values show the expected van't Hoff temperature dependence (Fig. 4(a)) with a sorption energy of −33 kJ/mol. Both the absolute values of the Henry constants and the sorption energy are quite close to the values determined previously for SF_6 in NaX zeolite (Doetsch and Ruthven, 1976).

The diffusivity values show the expected Arrhenius temperature dependence (Fig. 4(b)) with an activation energy of about 19 kJ/mol. The SF_6 diffusivity is comparable with that of propane and larger than that of n-hexane, which has a similar kinetic diameter

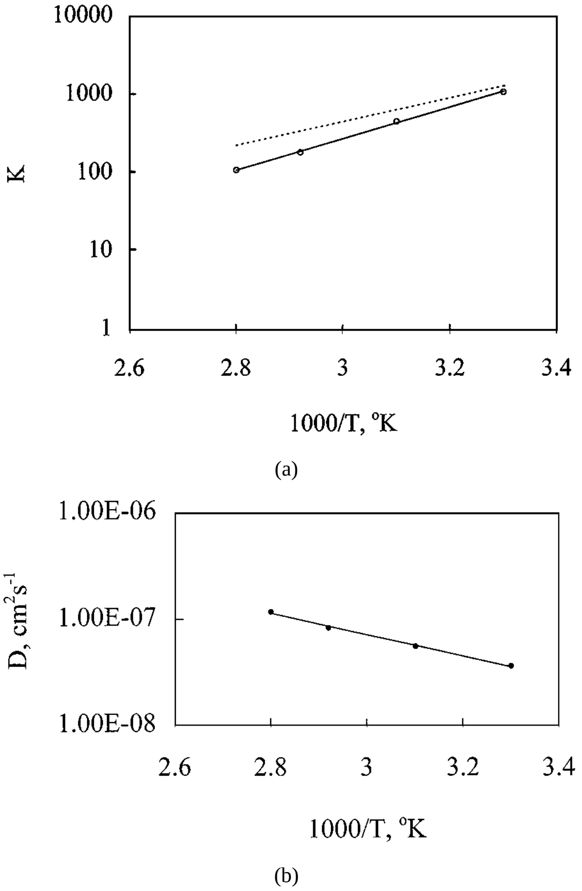

Figure 4. Temperature dependence of (a) dimensionless Henry constant (*K*) and (b) intracrystalline diffusivity (*D*). The broken line shows comparative Henry constant data for SF_6-NaX (Doetsch and Ruthven, 1976).

(Cavlacante and Ruthven, 1995). It appears that the near spherical shape of the SF_6 molecule is relatively more favorable for diffusive transport.

Conclusions

The product *KD* suggests a permeability, in an "ideal" zeolite crystal, at low loading, of about 1.7×10^{-9} mol/(cm · atm · s) at 298 K. The permeabilities of N_2 and H_2 in an apparently defect free silicalite membrane are about 7.5×10^{-9} mol/(cm·atm·s) at this temperature (Broeke et al., 1999) i.e. about four times the value for SF_6. Very much smaller SF_6 permeabilities and correspondingly larger N_2/SF_6 permeability ratios were reported by Baertsch et al. (1996) and Funke et al. (1997) but from the data presented here such values are difficult to explain unless the transport of SF_6 within the membrane is severely reduced by grain boundaries or some other form of interfacial resistance.

Nomenclature

c	Concentration of sorbate in effluent gas
c_0	Concentration of sorbate in equilibration gas
D	Intracrystalline diffusivity
F	Purge flow rate
K	Dimensionless adsorption equilibrium constant
L	Parameter defined by Eq. (3)
R	Equivalent radius of zeolite crystal
t	Time
V	Volume of zeolite sample
β	See Eq. (2)

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