R&D NOTES

Concentration Dependence of Surface Diffusion and Zeolitic Diffusion

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Surface diffusion, that is, diffusion of adsorbed molecules or atoms on surfaces, has long been investigated (Kapoor et al., 1989). Diffusion of sorbate in zeolite, called zeolitic diffusion, has attracted a special interest recently because of the increasing importance of zeolite in separation and catalysis. One of the most intriguing aspects of both surface diffusion and zeolitic diffusion is the strong dependence of diffusivity (Fickian diffusivity) on sorbate concentration. However, seemingly different concentration dependences have been observed for surface diffusion and zeolitic diffusion, and these dependences have been interpreted by different and unrelated theories (Yang, 1987).

Surface diffusivity increases with sorbate concentration. The HIO theory (Higashi, Itoh and Oishi, 1963) stipulates that $D/D_0 = 1/(1-\theta)$, where D is diffusivity, θ is fractional surface coverage, and D_0 is zero surface coverage. The HIO theory has been modified by Yang et al. (1973) to account for second-layer adsorption, and hence a slower rise of diffusivity with θ. To date, all observed concentration dependences of surface diffusivity follow the increasing trend (D increases with θ), although the opposite is possible if the sorbate-sorbate bond is stronger than the sorbate-surface bond, according to the model of Yang et al. (1973). The concentration dependence of zeolitic diffusion seems to be more complex and erratic; all possible types of dependence have been observed (Yang, 1987). In most of the published results, an increasing dependence similar to the HIO-type is seen. A popular interpretation of this dependence is based on Darken's theory (1948). However, lingering questions remain regarding the assumptions made in the derivation of the Darken-type theory (Yang, 1987) and, more important, on the origin of the concentration dependence of diffusivity.

In this note, we propose a unified model based on the random walk/hopping mechanism. This model is capable of interpreting both increasing and decreasing concentration dependences for both surface diffusion and zeolitic diffusion, and it sheds light on the origin of the concentration dependence for both kinds of diffusion.

Model Formulation

The kinetic approach adopted here follows the classical transition state theory, which has been used previously to study diffusion in zeolite (Riekert, 1971; Yeh and Yang, 1989). As depicted in Figure 1, the passing of molecule A through the intercavity aperture in zeolite or from one adsorption site to another may be considered as a rate process involving an activated transition state. The molecular migration is caused by a succession of random discrete jumps between neighboring sites, and a minimum activation energy is needed for each jump. Then, an adsorbate molecule A residing at lattice site x-$\delta/2$ may undergo the following processes:

Activation:

$$(A)_{x-\delta/2} \xrightarrow{k_a} (A^*)_{x-\delta/2} \qquad r_1 = k_a\theta_{A,x-\delta/2} \tag{1}$$

Deactivation:

$$(A^*)_{x-\delta/2} + (V)_{x-\delta/2} \xrightarrow{k_m} (A)_{x-\delta/2} \qquad r_2 = k_m\theta_{A^*,x-\delta/2}\,\theta_{v,x-\delta/2} \tag{2}$$

Forward Migration:

$$(A^*)_{x-\delta/2} + (V)_{x+\delta/2} \xrightarrow{k_m} (A)_{x+\delta/2} \qquad r_3 = k_m\theta_{A^*,x-\delta/2}\,\theta_{v,x+\delta/2} \tag{3}$$

Return Rate Due to Blockage by Another Adsorbate:

$$(A^*)_{x-\delta/2} + (A)_{x+\delta/2} \xrightarrow{k_b} (A)_{x-\delta/2} + (A)_{x+\delta/2} \qquad r_4 = k_b\theta_{A^*,x-\delta/2}\,\theta_{A,x+\delta/2} \tag{4}$$

The net rate for forward migration at lattice $(x - \delta/2)$ is:

$$M_{x-\delta/2} = k_m\theta_{A^*,x-\delta/2}\,\theta_{v,x+\delta/2} + \{H(k_m - k_b)\}(k_m - k_b)\theta_{A^*,x-\delta/2}\,\theta_{A,x+\delta/2} \tag{5}$$

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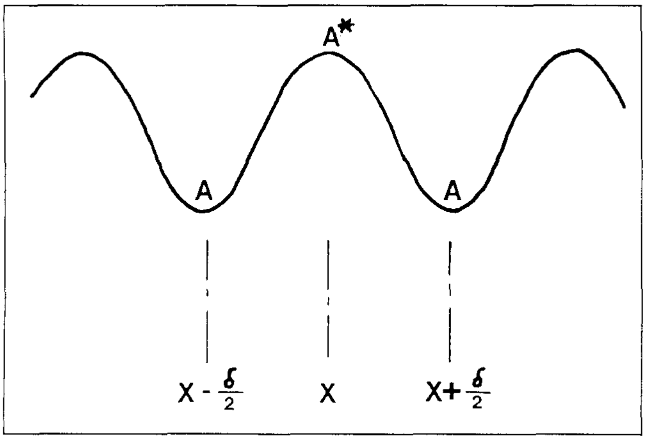

Figure 1. Potential energy along distance on surface of zeolite.

It is applicable to both cage and channel structures of zeolite, where A^* indicates an activated molecule located between two cavities or two adsorption sites.

where $H(k_m - k_b)$ is the Heaviside step function defined by:

$$H(k_m - k_b) = \begin{cases} 0 \text{ if } k_b \geq k_m \\ 1 \text{ if } 0 \leq k_b < k_m \end{cases}$$

The last term in Eq. 5 is the net rate of forward movement with the same forward rate constant k_m for both empty and occupied sites. The value of k_b may be greater than k_m. When $k_m > k_b$, there is a net forward movement even when the next site is occupied. When $k_b >> k_m$, nearly total blockage occurs. However, pore blockage cannot cause negative movement; rather, the activated sorbate molecule stays at its original site. Therefore, the second term in Eq. 5 cannot be negative, even though k_b can be greater than k_m.

Following the same procedure, one gets the total net backward migration at lattice $(x + \delta/2)$:

$$M_{x+\delta/2} = k_m \theta_{A^*,x+\delta/2} \theta_{v,x-\delta/2} + \{H(k_m - k_b)\} (k_m - k_b) \theta_{A^*,x+\delta/2} \theta_{A,x-\delta/2} \quad (6)$$

The net formation rates of activated complex are:

$$\frac{\partial \theta_{A^*,x-\delta/2}}{\partial t} = k_a \theta_{A,x-\delta/2} - k_m \theta_{A^*,x-\delta/2} \theta_{v,x-\delta/2} - k_m \theta_{A^*,x-\delta/2} \theta_{v,x+\delta/2} - k_b \theta_{A^*,x-\delta/2} \theta_{A,x+\delta/2} \quad (7)$$

$$\frac{\partial \theta_{A^*,x+\delta/2}}{\partial t} = k_a \theta_{A,x+\delta/2} - k_m \theta_{A^*,x+\delta/2} \theta_{v,x+\delta/2} - k_m \theta_{A^*,x+\delta/2} \theta_{v,x-\delta/2} - k_b \theta_{A^*,x+\delta/2} \theta_{A,x-\delta/2} \quad (8)$$

A steady-state analysis for the activated complex yields:

$$\theta_{A^*,x-\delta/2} = \frac{k_a \theta_{A,x-\delta/2}}{k_m (\theta_{v,x-\delta/2} + \theta_{v,x+\delta/2}) + k_b \theta_{A,x+\delta/2}} \quad (9)$$

$$\theta_{A^*,x+\delta/2} = \frac{k_a \theta_{A,x+\delta/2}}{k_m (\theta_{v,x-\delta/2} + \theta_{v,x+\delta/2}) + k_b \theta_{A,x-\delta/2}} \quad (10)$$

The net rate of migration is:

$$r_{\text{net}} = M_{x-\delta/2} - M_{x+\delta/2} \quad (11)$$

If the lattice parameter δ is sufficiently small, one may approximate:

$$\theta_{A,x-\delta/2} = \theta_{A,x} - \frac{\delta}{2} \frac{\partial \theta_{A,x}}{\partial x} \quad (12)$$

$$\theta_{A,x+\delta/2} = \theta_{A,x} + \frac{\delta}{2} \frac{\partial \theta_{A,x}}{\partial x} \quad (13)$$

with similar approximations for $\theta_{v,x-\delta/2}$ and $\theta_{v,x+\delta/2}$. Moreover,

$$\theta_{A,x} + \theta_{v,x} = 1 \quad (14)$$

Finally, the mass flux can be related to the rate of migration via

$$J(A_c) = r_{\text{net}} (V_c) \quad (15)$$

or

$$J = \delta r_{\text{net}}$$

Substituting Eqs. 5, 6, and 9-14 into Eq. 15, and comparing the result with the Fickian form:

$$J = -D \frac{\partial \theta_{A,x}}{\partial x} \quad (16)$$

and letting $\theta_{A,x} = \theta$, one gets the following expression for the Fickian diffusivity:

$$D = k_m k_a \delta^2 \frac{k_m(1-\theta) + \frac{k_b}{2} \theta(2-\theta) + H(k_m - k_b) \frac{(k_m - k_b)}{k_m} \frac{k_b}{2} \theta^2}{2 \left[k_m(1-\theta) + \frac{k_b}{2} \theta \right]^2} \quad (17)$$

From Eq. 17, the diffusivity at $\theta = 0$ is

$$D_o = \lim_{\theta \to 0} D = \frac{k_a \delta^2}{2} \quad (18)$$

Let

$$\lambda = \frac{k_b}{k_m} \quad (19)$$

one gets the concentration dependence:

$$\frac{D}{D_o} = \frac{1 - \theta + \frac{\lambda}{2} \theta(2-\theta) + H(1-\lambda)(1-\lambda) \frac{\lambda}{2} \theta^2}{\left(1 - \theta + \frac{\lambda}{2} \theta\right)^2} \quad (20)$$

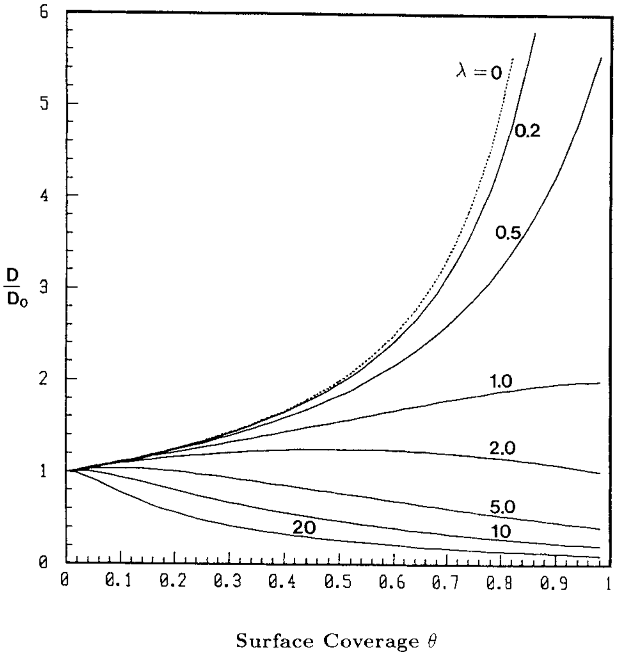

Figure 2. Concentration dependence of surface and zeolitic diffusions.

λ = blockage parameter; λ = 0 for surface diffusion; λ > 0 for zeolitic diffusion.

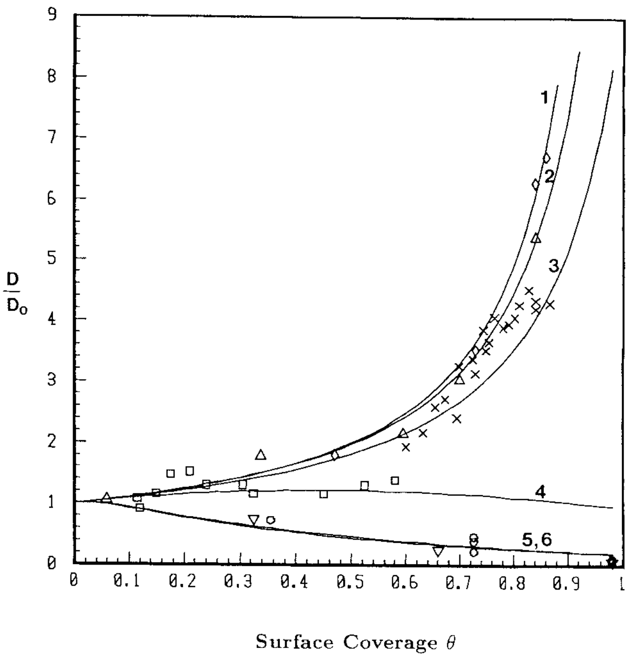

Figure 3. Case 1 for surface diffusion and cases 2-6 for zeolitic diffusion (see Table 1).

Discussion

Equation 20 is the relationship describing the concentration dependence of diffusivity. This relationship is applicable to diffusion in zeolite—in both zeolites with cavity and channel structures, as well as surface diffusion. Clearly, λ is the distinguishing parameter for different gas-solid systems.

The value of λ indicates the degree of blockage by another adsorbed molecule. We first consider two extreme cases.

Case 1. Large molecules diffuse in a zeolite with a channel structure, such as ZSM-5 and clinoptilolite. When the molecular dimension approaches the channel opening, one expects strong blockage and a large value of λ.

Case 2. In surface diffusion, no blockage is expected due to the unlimited space, therefore λ = 0. For λ = 0, Eq. 20 becomes:

$$\frac{D}{D_o}=\frac{1}{1-\theta} \tag{21}$$

which is identical to the HIO model (1963), as well as the Darken model that is unrelated to the HIO model (Yang, 1987).

Equation 20 is plotted on Figure 2 at different λ values. λ = 0 is for surface diffusion, and larger λ is for very restricted diffusion. These are the two bounds for zeolitic diffusion.

Experimental data on surface diffusion and zeolitic diffusion from the literature are compared with Eq. 20 on Figure 3. Here, λ becomes a fitting parameter, with the values for λ listed in Table 1. However, as already discussed, λ is a blockage parameter, whose value indicates the degree of pore blocking by the adsorbate. For a molecule hopping onto a site that is occupied, λ is the ratio of probabilities of bouncing backward over bouncing forward. Proximity of the sizes of adsorbate and zeolite channel/pore should result in large λ values. The cases of benzene in ZSM-5 (Qureshi and Wei, 1990) and triethylamine in 13X (Karger and Ruthven, 1981) are examples where large λ values are expected and indeed observed as shown in Figure 3 and Table 1.

The model proposed here should also be applicable to the dependence of diffusivity on the adsorption of another species. Influence of diffusion in zeolites by another sorbate has already been reported in the literature: diffusion of N_2 and CH_4 in 4A zeolite (Habgood, 1958); diffusion of SO_2 in mordenite

Table 1. Experimental Data Fitted by Model (See Figure 3)

Curve No.	Sorbate	Sorbent	Diffusion Type	Temperature	λ Value	Reference
1	SO_2	Vycor Glass	Surface	15°C	0	Gilliland et al. (1974)
2	C_2H_6	4A	Zeolitic	50°C	0.193	Yeh (1989)
3	Propane	5A	Zeolitic	50°C	0.305	Ruthven and Loughlin (1971)
4	Benzene	ZSM-5	Zeolitic	65°C	2.11	Qureshi and Wei (1990)
5	Triethylamine	13X	Zeolitic	190°C	10.2	Karger and Ruthven (1981)
6	Triethylamine	13X	Zeolitic	160°C	10.8	Karger and Ruthven (1981)

with water adsorbed (Roux and Ma, 1973); and diffusion of N_2 in 5A zeolite with CO_2 adsorbed (Chihara et al., 1991). It is difficult to explain the cross-species dependence by the Darken-type model, since this model would predict an increasing diffusivity of A in the presence of B while much of the experimental results show an opposite trend.

Two other factors also influence the concentration dependence of diffusivity: (1) surface energetic heterogeneity, as discussed previously by Kapoor and Yang (1990); and (2) adsorbate-adsorbate interactions, as discussed by Yang et al. (1973).

Conclusion

A unified kinetic model based on random walk is formulated for both surface diffusion and zeolitic diffusion. Concentration dependence of diffusivity is expressed by Eq. 20, where λ, a pore or site blockage parameter, is the distinguished parameter: $\lambda = 0$ for surface diffusion and $\lambda > 0$ for zeolitic diffusion. Proximity between the size or adsorbate molecule and the channel/pore size yields large λ values. The basis of the model is the common origin of the concentration dependence for both surface diffusion and zeolitic diffusion.

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Notation

A = adsorbate
A_c = cross-sectional area of cavity or channel
D = Fickian diffusivity
D_0 = Fickian diffusivity at zero surface coverage
$H(z)$ = Heaviside function, 1 for $z > 0$ and 0 for $z \leq 0$
J = flux
k_a = rate constant of activation
k_b = rate constant of blockage; rate constant of returning to original site due to another adsorbate
k_m = rate constant of forward migration
M = rate of migration
r = rate
t = time
V = vacancy or vacant site
V_c = volume of cavity or unit volume of channel
x = distance

Greek letters

δ = length per cavity or unit length of channel
λ = k_b/k_m, a blockage parameter
θ = fractional surface coverage

Subscripts

A = adsorbate
A^* = activated adsorbate
v = vacant site

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