Surface Diffusion of Multilayer Adsorbed Species

Y. D. Chen and R. T. Yang
Dept. of Chemical Engineering, State University of New York at Buffalo, Buffalo, NY 14260

A model based on kinetic theory is derived for surface diffusion of multilayer adsorbed species on a homogeneous surface. A simple solution is obtained for expressing the concentration dependence of surface diffusivity. For monolayer adsorbate, the solution is reduced to the classical HIO model. This solution, in principle, requires no fitting parameters and is capable of predicting the unique concentration dependent behavior exhibited by multilayer surface diffusion, where the diffusivity first increases with surface concentration to a maximum followed by a decrease. Seventeen sets of experimental data from the literature are used to test the model, with fair results. It is also shown that heats of adsorption can be calculated from multilayer surface diffusivity data by using this model.

Introduction

Diffusion of adsorbed molecules on solid surfaces is an activated process involving activation and hopping of the molecules on specific sites on the surface. Surface diffusion makes an important contribution to the mass transfer in porous media and can be the rate-controlling step in many processes in adsorption and catalysis. Reviews of the vast literature on the subject are available (Ehrlich, 1980; King, 1980; Kapoor et al., 1989). A uniquely interesting phenomenon associated with surface diffusion is its concentration dependence: the (Fickian) diffusivity first increases with concentration (usually within the monolayer coverage) followed by a decrease. This phenomenon has been addressed in a number of studies (Gilliland et al., 1958, 1974; Higashi et al., 1963; Roybal and Sandler, 1972; Yang et al., 1973; Komiyama and Smith, 1974; Sudo et al., 1978; Suzuki and Fujii, 1982; Tamon et al., 1985; Worch and Zapke, 1985; Itaya et al., 1987; Yang, 1987; Sun and Meunier, 1987; Friedrich et al., 1989; Seidel and Carl, 1989; Chen and Yang, 1991, 1992; Kapoor and Yang, 1991; Hu et al., 1993). Molecular dynamics or time-dependent Monte Carlo simulation can also yield information on the concentration dependence of diffusion on both open surface and micropores (Magda et al., 1985; Allen and Tildesley, 1988; Bowler and Hood, 1990; June et al., 1990; Arena et al., 1991).

The vast majority of the physical adsorption systems (that is, gas-solid pairs) involves multilayer adsorption (that is, multilayer buildup before a complete monolayer is formed). This is reflected in the shape of type II isotherm, which represents most of the gas-solid systems. A quantitative description of multilayer physical adsorption is given by the BET theory (Brunauer et al., 1938), which remains to be most useful for representing type II isotherms. Despite the presence of multilayer adsorption, diffusion on multiadsorbed layers has not been considered in previous studies. This is the first study on diffusion on multiadsorbed layers. Results from the BET theory are used in this formulation. The result of this study is a simple model, which is capable of interpreting the unique increase-decrease concentration dependence of surface diffusion.

Model Formulation

The kinetic approach adopted here follows the classical transition state theory, which has been used previously for studying surface diffusion and diffusion in zeolite (Riekert, 1971; Yeh and Yang, 1989; Chen and Yang, 1991, 1992). As depicted in Figure 1, the migration of an adsorbed molecule may be considered as involving a hopping mechanism from site to site. This is a rate process involving an activated transition state, A^*. The migration under consideration is in the x direction only. There are many adsorption sites at any given location in the x direction, and a distribution of multilayer absorbed molecules is allowed at each location.

Two simplifying assumptions are made. First, only molecules on the topmost layer at each site can be activated and hop. Second, the gas-solid system is at a pseudo-steady state, that is, steady state on a local scale but not on a global scale. The surface area covered only by 0, 1, 2, ..., n layers of adsorbed molecules is represented by S_0, S_1, S_2, ..., S_n. Under the pseudo-steady state assumption, the S_i distribution is dom-

---

Correspondence concerning this article should be addressed to R. T. Yang.

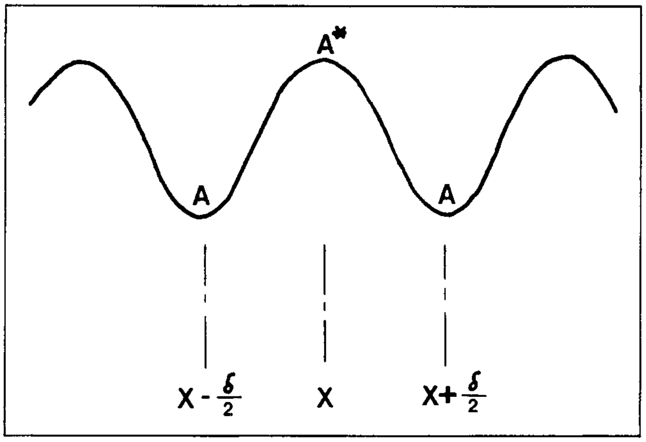

Figure 1. Potential energy along distance on surface, where δ is distance between two adsorption sites, and A^* is an activated molecule.

inated by gas-solid equilibrium, and the gas-phase concentration remains constant. This is a reasonable assumption when one is considering surface diffusion which is not caused by diffusion in the gas phase above the surface. The assumption that the S_i distribution is dominated by gas-phase concentration is also justified by the fact that the energy for desorption is considerably higher than the activation energy for surface diffusion. The S_i distribution is given by the BET theory. As in the BET theory, the S_i distribution is a constant and is followed at any given site location along the x direction.

The molecules at sites located at $x-(\delta/2)$ undergo the following rate processes:

Rate of activation at different layers:

$$\begin{aligned} r_{a1} &= \frac{S_1}{A} k_{a1} q_{x-\frac{\delta}{2}} \\ r_{a2} &= \frac{S_2}{A} k_{a2} q_{x-\frac{\delta}{2}} \\ &\vdots \\ r_{an} &= \frac{S_n}{A} k_{an} q_{x-\frac{\delta}{2}} \end{aligned} \tag{1}$$

where the numeral subscript denotes the number of layer, k is the rate constant, q is the amount adsorbed, and A is the total surface area.

Rate of deactivation of the activated molecule:

$$\begin{aligned} r_{1,x\mp\frac{\delta}{2}} &= \frac{S_0}{A} k_{d0} q^*_{x-\frac{\delta}{2}} q^v_{x\mp\frac{\delta}{2}} \\ r_{2,x\mp\frac{\delta}{2}} &= \frac{S_1}{A} k_{d1} q^*_{x-\frac{\delta}{2}} q_{x\mp\frac{\delta}{2}} \\ &\vdots \\ r_{n,x\mp\frac{\delta}{2}} &= \frac{S_{n-1}}{A} k_{d(n-1)} q^*_{x-\frac{\delta}{2}} q_{x\mp\frac{\delta}{2}} \end{aligned} \tag{2}$$

where q^* is the concentration of the activated molecule which lands on either site at $x-(\delta/2)$ or $x+(\delta/2)$.

The total surface area is given by:

$$A = \sum_{i=0}^{n} S_i \tag{3}$$

As in the BET derivation, the energetics for layers above the second are the same. It follows then:

$$\text{For activation: } k_{a2} = k_{a3} = \cdots = k_{an} \tag{4}$$

$$\text{For deactivation: } k_{d1} = k_{d2} = \cdots = k_{d(n-1)} \tag{5}$$

The distribution of layers, S_i, is given by the BET theory:

$$\begin{aligned} S_2 &= \beta S_1 \\ S_3 &= \beta^2 S_1 \\ &\vdots \\ S_n &= \beta^{n-1} S_1 \end{aligned} \tag{6}$$

where β is a distribution parameter and $\beta \leq 1$.

The rates of forward migration on the ith layer at location $x-(\delta/2)$ are given by:

$$\left(M_{x-\frac{\delta}{2}}\right)_i = \frac{S_{i-1}}{A} k_{d(i-1)} q^*_{x-\frac{\delta}{2}} q_{x+\frac{\delta}{2}} \quad i \neq 1 \tag{7}$$

$$M_{x-\frac{\delta}{2}} = \frac{S_0}{A} k_{d0} q^*_{x-\frac{\delta}{2}} q^v_{x+\frac{\delta}{2}} \quad i = 1 \tag{8}$$

Similar expressions can be written for the rates of backward migration at location $x+(\delta/2)$:

$$\left(M_{x+\frac{\delta}{2}}\right)_i = \frac{S_{i-1}}{A} k_{d(i-1)} q^*_{x+\frac{\delta}{2}} q_{x-\frac{\delta}{2}} \quad i \neq 1 \tag{9}$$

$$M_{x+\frac{\delta}{2}} = \frac{S_0}{A} k_{d0} q^*_{x+\frac{\delta}{2}} q^v_{x-\frac{\delta}{2}} \quad i = 1 \tag{10}$$

The rate of formation of the activated molecule is:

$$\begin{aligned} \frac{\partial q^*_{x-\frac{\delta}{2}}}{\partial t} &= r_{a1} + r_{a2} + \cdots + r_{an} \\ &- \left(r_{1,x-\frac{\delta}{2}} + r_{1,x+\frac{\delta}{2}} + r_{2,x-\frac{\delta}{2}} + r_{2,x+\frac{\delta}{2}} + \cdots + r_{n,x-\frac{\delta}{2}} + r_{n,x+\frac{\delta}{2}} \right) \end{aligned} \tag{11}$$

a symmetrical expression can be written for $[\partial q^*_{x+(\delta/2)}]/\partial t$.

If the intersite distance δ is sufficiently small, one may approximate:

$$q_{x\pm\frac{\delta}{2}} = q \pm \frac{\delta}{2} \frac{\partial q}{\partial x} \tag{12}$$

$$q^v_{x\pm\frac{\delta}{2}} = q^v \pm \frac{\delta}{2} \frac{\partial q^v}{\partial x} \tag{13}$$

Using the steady-state assumption:

$$\frac{\partial q^*_{x-\frac{\delta}{2}}}{\partial t}=\frac{\partial q^*_{x+\frac{\delta}{2}}}{\partial t}=0 \tag{14}$$

one obtains the concentrations of the activated molecule:

$$q^*_{x\mp\frac{\delta}{2}}=\frac{S_1\left[k_{a1}+k_{a2}\,\frac{\beta(1-\beta^{n-1})}{1-\beta}\right]q_{x\mp\frac{\delta}{2}}}{2S_0k_{d0}q^v+2S_1k_{d1}q\,\frac{1-\beta^{n-1}}{1-\beta}} \tag{15}$$

The net rate of forward migration across point x on the ith layer is given by:

$$(r_{\rm net})_i=\left(M_{x-\frac{\delta}{2}}\right)_i-\left(M_{x+\frac{\delta}{2}}\right)_i$$

$$=\frac{S_{i-1}}{A}\,k_{d(i-1)}\left(q^*_{x-\frac{\delta}{2}}q_{x+\frac{\delta}{2}}-q^*_{x+\frac{\delta}{2}}q_{x-\frac{\delta}{2}}\right)=0 \qquad i\neq 1 \tag{16}$$

and for $i=1$:

$$r_{\rm net}=\frac{S_0}{A}\,k_{d0}\left(q^*_{x-\frac{\delta}{2}}q^v_{x+\frac{\delta}{2}}-q^*_{x+\frac{\delta}{2}}q^v_{x-\frac{\delta}{2}}\right)$$

$$=\frac{S_0S_1k_{a1}k_{d0}\delta\left[1+\frac{k_{a2}}{k_{a1}}\,\frac{\beta(1-\beta^{n-1})}{1-\beta}\right]}{2A\left(S_0k_{d0}q^v+S_1k_{d1}q\,\frac{1-\beta^{n-1}}{1-\beta}\right)}\left[q\,\frac{\partial q^v}{\partial x}-q^v\,\frac{\partial q}{\partial x}\right] \tag{17}$$

Moreover, q and q^v can be related by:

$$q_m=q_0A=q_0\sum_{i=0}^{n}S_i=q^v+\frac{\Sigma_{i=1}^nS_i}{\Sigma_{i=1}^n iS_i}\,q=q^v+\frac{(1-\beta)(1-\beta^n)}{1-(1+n)\beta^n+n\beta^{n+1}}\,q \tag{18}$$

where $q=q_0\,\Sigma_{i=0}^n\,iS_i$. q_0 is the adsorbed monolayer amount per unit surface area. q_m is the amount adsorbed when the entire surface is covered by a complete monolayer.

In deriving Eqs. 15 and 18, the following manipulations are used:

$$\sum_{i=1}^{n}S_i=S_1(1+\beta+\cdots+\beta^n)=S_1\,\frac{1-\beta^n}{1-\beta}$$

$$\sum_{i=1}^{n}iS_i=S_1(1+2\beta+\cdots+n\beta^{n-1})$$

$$=S_1\,\frac{d}{d\beta}\,(\beta+\beta^2+\cdots+\beta^n)$$

$$=S_1\,\frac{1-n\beta^n-\beta^n+n\beta^{n+1}}{(1-\beta)^2}$$

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

$$JS_i=A\delta(r_{\rm net})_i \tag{19}$$

or

$$J=\frac{A}{\Sigma_{i=1}^nS_i}\,\delta r_{\rm net}=\frac{A\delta r_{\rm net}}{S_1\left(\frac{1-\beta^n}{1-\beta}\right)} \tag{20}$$

Substituting Eqs. 17 and 18 into Eq. 20, and comparing the result with the Fickian form:

$$J=-D\,\frac{\partial q}{\partial x} \tag{21}$$

one gets the following expression for the surface diffusivity:

$$D=\frac{k_{a1}\delta^2\left[1+\frac{k_{a2}}{k_{a1}}\,\frac{\beta(1-\beta^{n-1})}{1-\beta}\right]\frac{1-\beta}{1-\beta^n}}{2\left[1-\frac{(1-\beta)(1-\beta^n)}{1-(1+n)\beta^n+n\beta^{n+1}}\,\theta+\frac{S_1k_{d1}}{S_0k_{d0}}\,\frac{1-\beta^{n-1}}{1-\beta}\,\theta\right]} \tag{22}$$

where surface coverage $\theta=(q/q_m)$. As $\theta\to 0$, β also approaches zero as stipulated by the BET theory. One obtains the surface diffusivity at zero coverage:

$$D_0=\lim_{\theta\to 0}D=\frac{1}{2}\,k_{a1}\delta^2 \tag{23}$$

This is the Einstein equation for diffusivity.

Since:

$$\frac{q^v}{S_0}=\frac{q}{\Sigma_{i=1}^n iS_i} \tag{24}$$

and from Eq. 18, one gets:

$$\frac{S_1}{S_0}=\frac{1-\beta}{1-\beta^n}\,\frac{q_m-q^v}{q^v} \tag{25}$$

Substituting q^v from Eq. 18 and noting $\theta=q/q_m$,

$$\frac{S_1}{S_0}=\frac{(1-\beta)^2\theta}{1-(1+n)\beta^n+n\beta^{n+1}-(1-\beta)(1-\beta^n)\theta} \tag{26}$$

Finally, by substituting Eqs. 23 and 26 into Eq. 22, one obtains the general equation for multilayer surface diffusivity:

$$\frac{D}{D_0}=\frac{\left(1+\frac{1}{\alpha}\frac{\beta(1-\beta^{n-1})}{1-\beta}\right)\frac{1-\beta}{1-\beta^n}}{1-\frac{(1-\beta)(1-\beta^n)}{1-(1+n)\beta^n+n\beta^{n+1}}\theta+\frac{\alpha(1-\beta)(1-\beta^{n-1})\theta^2}{1-(1+n)\beta^n+n\beta^{n+1}-(1-\beta)(1-\beta^n)\theta}} \tag{27}$$

On an open surface, $n\rightarrow\infty$, then Eq. 27 reduces to:

$$\frac{D}{D_0}=\frac{1-\beta+\frac{\beta}{\alpha}}{1-(1-\beta)\theta+\frac{\alpha(1-\beta)\theta^2}{1-(1-\beta)\theta}} \tag{28}$$

In Eqs. 27 and 28, α is the ratio of the rate constants between the first adsorbed layer and the higher adsorbed layers, and is defined by:

$$\alpha=\frac{k_{d1}}{k_{d0}}=\frac{k_{a1}}{k_{a2}}=e^{-(E_1-E_2)/RT}=e^{-\Delta E/RT} \tag{29}$$

where E_1 is the activation energy for surface diffusion on the first layer, that is, on bare surface, and E_2 is that on higher layers, that is, on liquid.

Discussion

Equations 23 and 28 yield the values for multilayer surface diffusivities. Of particular interest is the concentration dependence of surface diffusivity, which is predicted by Eq. 28.

Equation 28 contains two parameters, α and β. In what follows we will show that both α and β can be evaluated independently; hence, Eq. 28 contains no fitting parameters.

The value of α is given by Eq. 29. The value of the activation energy for surface diffusion on the second and higher layers, E_2, can be obtained, in principle, from the temperature dependence of viscosity, μ_L, of the adsorbed molecule in the liquid state (Frenkel, 1955).

$$\mu_L=KTe^{E_2/RT} \tag{30}$$

However, it is not possible to predict the activation energy for surface diffusion on bare surface, E_1, without knowledge of the sorbent-sorbate interaction properties. There are, nevertheless, many empirical and semi-empirical correlations between activation energy for surface diffusion E_1 and heat of adsorption H_1 (Roybal et al., 1972; Gilliland et al., 1974; Sladek et al., 1974; King, 1980). The heat of adsorption is readily measurable from equilibrium isotherm. Therefore, the activation energy for surface diffusion on bare surface E_1 can be calculated. Finally, the diffusivity at zero surface coverage, D_0, can be estimated from Eq. 23 which can be rewritten as:

$$D_0=\frac{1}{2}\left(\frac{KT}{h}\right)\delta^2e^{-E_1/RT} \tag{31}$$

where K is the Boltzmann constant and h is the Planck constant. Further discussions on α will be given in the subsequent sections. The value of β is related to the surface coverage, θ, by the BET equation:

$$\theta=\frac{c\beta}{(1-\beta)(1-\beta+c\beta)} \tag{32}$$

where c is a constant in the BET equation and is given by (Brunauer et al., 1938):

$$c\approx e^{(H_1-H_2)/RT}=e^{\Delta H/RT} \tag{33}$$

Here, H_1 and H_2 are the absolute values of heats of adsorption on bare surface and on second and higher layers, respectively. For homogeneous surfaces and negligible lateral sorbate-sorbate interactions, both α and c are constants, being independent of θ. The value of c is indeed a constant for many gas-solid systems as indicated by the good fit with the BET isotherm equation and can be calculated once the isotherm data are available. Consequently, Eq. 32 (by which β is related to θ) can be used in conjunction with Eq. 28 to predict the concentration dependence of surface diffusivity. Following this discussion, the model, Eq. 28, has no fitting parameters; the concentration dependence of multilayer surface diffusion is thus predictable.

Concentration dependence and limiting cases

By inspecting Eq. 28, qualitative features of the concentration dependence can be obtained. It is recalled that $\beta\leq1$. Equation 29 shows that α approaches zero for gas-solid systems with strong sorbate-surface interactions, and it approaches unity for weak sorbate-surface interactions. Thus, $0<\alpha<1$. When surface coverage, θ, is small, Eq. 28 predicts that D/D_0 increases with θ. Upon further increase in θ, D/D_0 will reach a maximum and eventually decrease. The value of θ, where surface diffusivity reaches a maximum, is obtained by equating the derivative of Eq. 28 to zero, where β is related to θ in the implicit form given by Eq. 32 with α and c as two parameters.

If α and c are related, one can solve Eqs. 28 and 32 numerically in the manner described above to obtain the value of θ, where D reaches a maximum. The parameter α is related to the activation energies for surface diffusion via Eq. 29. It has been suggested that the activation energy for surface diffusion is a fraction of the heat of adsorption (Robell et al., 1964). An empirical correlation has been obtained between the activation energy (E) and (the absolute value of) heat of adsorption (H):

$$E=\frac{H}{m} \tag{34}$$

The values of m have been found to be integers varying from 1 to 3 (Sladek et al., 1974). Using this empirical relationship and assuming that $H_2\ll H_1$, the relationship between α and c can be obtained from Eqs. 29 and 33. The numerical solutions for the θ values where D reaches maximum are shown in Figure

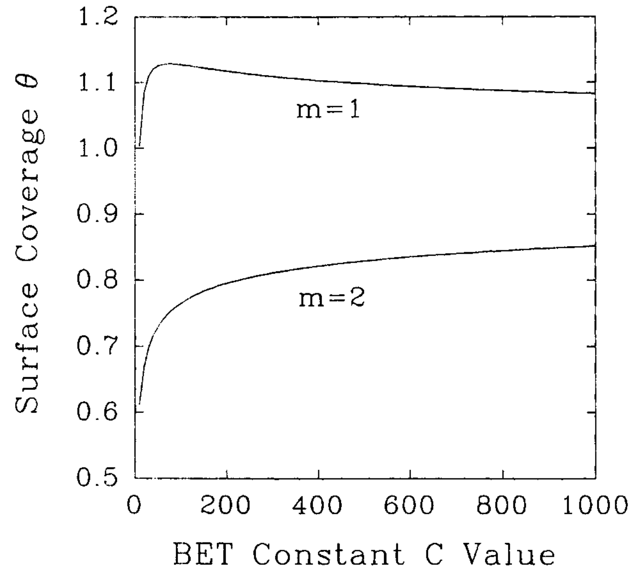

Figure 2. Surface coverage where surface diffusivity reaches its maximum value.

2, for m taking the most common values of 1 and 2 (Sladek et al., 1974). It shows that the θ values for maximal D are always below 1.14, which agrees with all observed experimental results as will be shown shortly.

Two limiting cases for Eqs. 27 and 28 can be obtained. Monolayer surface diffusion is considered first. A large body of literature exists on the subject of surface diffusion in monolayer adsorbates (Yang, 1987). The solution for monolayer surface diffusion can be obtained by substituting $n=1$ into the general solution, Eq. 27, which yields:

$$\frac{D}{D_0}=\frac{1}{1-\theta} \tag{35}$$

This solution is identical to that of the HIO model (Higashi et al., 1964).

Another limiting case pertains to $\beta \rightarrow 1$. By combining Eqs. 28 and 32, and taking the limit, one finds

$$\frac{D}{D_0}\rightarrow 0 \tag{36}$$

Comparison with experimental data

Experimental data on surface diffusivities are not scarce (Kapoor et al., 1989). There, however, are not many complete data on surface diffusivity as a function of surface concentration.

The concentration dependence for multilayer surface diffusion (Eq. 28) differs from that for monolayer diffusion (Eq. 35). For a given gas-solid system, one needs to first determine whether the adsorption is monolayer or multilayer. This can be determined readily from the isotherm data. Two typical sets of isotherm data are shown in Figure 3. The CO_2/Carbolac (carbon) system exhibits type I isotherm, which is fitted by the Langmuir isotherm. Here, the adsorbed layer is monolayer. For the CF_2Cl_2/Carbolac (carbon) system, a typical type II isotherm is shown, hence the adsorbed layer is multilayer.

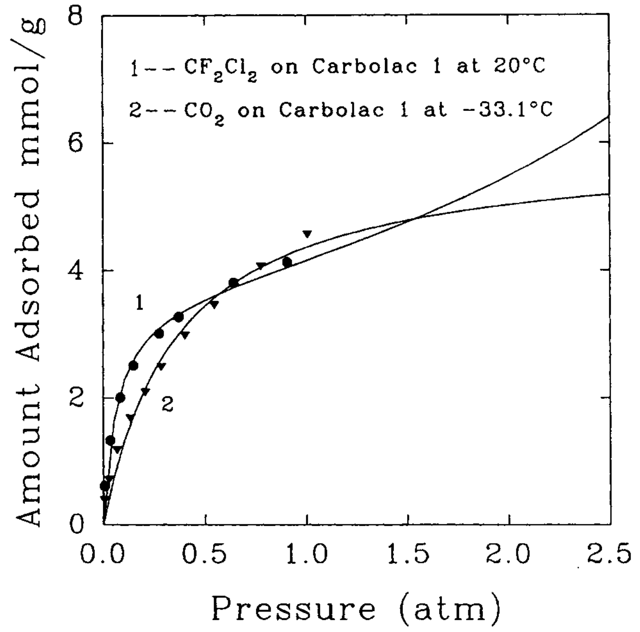

Figure 3. Adsorption isotherm for CO_2 on Carbolac carbon at −33.1°C showing Langmuir monolayer isotherm and CF_2Cl_2 on Carbolac carbon at 40°C showing BET multilayer isotherm (Carmen and Raal, 1951).

Seventeen sets of experimental data have been taken from the literature for comparison with the theory. These systems are listed in Table 1. For groups 1-10 (Table 1), complete adsorption isotherm data are available, from which the BET constant c can be calculated. Groups 1, 2, and 7 exhibit Langmuir isotherm, hence the monolayer Langmuir constants, b, instead of c, are calculated, and the HIO model, Eq. 35, will be used to predict concentration dependence. Once the BET constant is known, β becomes a known function of θ, as expressed by Eq. 32, and these β values will be used in Eq. 28. For groups 10-17 (Table 1), complete isotherm data are not available, hence β (and consequently c) becomes a fitting parameter in Eq. 28.

As described in the foregoing, the activation energy for surface diffusion can be related to the heat of adsorption by Eq. 34. Since this is empirical, however, we have not used this relationship to predict the values of α. Therefore, in the following comparison, we resort to using α as a fitting parameter. To summarize, for groups 1-10, c is known (hence β is known), so α is the only fitting parameter; for groups 11-17, both c and α are fitting parameters.

The data from groups 1-10 are shown in Figures 4 and 5. Groups 1, 2 and 7 exhibit Langmuir behavior, hence their concentration dependence is predicted by Eq. 35 for monolayer. The other groups exhibit multilayer adsorption isotherms, hence Eq. 28 is used. The values of α resulting from data fitting are also given in Table 1. Data from groups 11-17 are also correlated with Eq. 28, with resulting values of c and α in Table 1.

In all correlations, the surface concentration is expressed in surface coverage, θ. An interesting phenomenon in the con-

Table 1. Gas-Solid Systems Tested and Fitting Parameters

No.	Sorbate	Sorbent	Temp. °C	q_m mmol/g	c or b^* (torr^{-1})	$D_0 \times 10^5$ cm^2/s	$\alpha \times 10^2$	Reference
1	CO_2	Carbolac 1	−21.5	4.79	3.08×10^{-3}	4.989		Carman & Raal (1951)
2	CO_2	Carbolac 1	−33.1	5.93	3.63×10^{-3}	4.097		Carman & Raal (1951)
3	CO_2	Glass	−50	1.288	72.65	1.871	3.871	Gilliland et al. (1974)
4	CF_2Cl_2	Carbolac 1	20	3.582	87.58	1.418	2.972	Carman & Raal (1951)
5	NH_3	Glass	40	2.175	793.4	0.298	0.522	Gilliland et al. (1974)
6	NH_3	Glass	25	2.175	810.4	0.152	0.384	Gilliland et al. (1974)
7	C_3H_6	Glass	40	0.508	3.12×10^{-3}	13.32		Gilliland et al. (1958)
8	C_3H_6	Glass	0	0.591	43.73	3.478	3.333	Gilliland et al. (1958)
9	C_4H_{10}	Carbon	41.7	0.352	69.01	29.25	1.934	Ross & Good (1958)
10	C_4H_{10}	Carbon	30	0.352	89.25	18.85	1.905	Ross & Good (1958)
11	Ar	Silica	−184.1	2.868	21.53	0.486	4.645	Haul et al. (1958)
12	Ar	Silica	−195.6	2.868	25.11	0.289	3.983	Haul et al. (1958)
13	N_2	Spheron	−195.6	0.829	289.4	7.918	1.652	Haul et al. (1958)
14	C_6H_6	Aerosil	51.8		1.781	1.33	56.2	Haul et al. (1968)
15	C_6H_6	Aerosil	39.6		2.073	1.01	48.3	Haul et al. (1968)
16	C_6H_6	Aerosil	30.2		2.433	0.818	41.1	Haul et al. (1968)
17	C_6H_6	Aerosil	18.4		3.244	0.566	30.8	Haul et al. (1968)

*Groups 1, 2 and 7 exhibit monolayer adsorption.

centration dependence of surface diffusion is that the peak position of diffusivity can be well below $\theta = 1$, although more frequently, at θ near or above 1. The theoretical model result is capable of interpreting this behavior. The fittings in Figures 4-7 are indeed satisfactory.

The values of α and c may be compared. They are given by Eqs. 29 and 33, respectively. Since the activation energy for surface diffusion is less than the heat of adsorption, it follows then

$$\alpha \geq \frac{1}{c} \tag{37}$$

The values of α and c shown in Table 1 indeed follow this order for all cases.

From D_0 at two temperatures, the activation energy for diffusion on the first layer, E_1, can be obtained. With the value of α, the activation energy for higher-layer diffusion, E_2, can be calculated from Eq. 29. These values are listed in Table 2. Information on heats of adsorption may also be obtained from equilibrium isotherm or surface diffusivity data. It is first assumed that the heat of adsorption on second and higher layers (H_2) approaches the heat of condensation. One may then calculate the heat of adsorption on the first layer (H_1) from the value of c which can be obtained from the equilibrium isotherm or surface diffusivity data, as discussed. The values of H_1 and H_2 obtained in this manner are listed in Table 2. Where available, the experimental values of H_1 and H_2, denoted

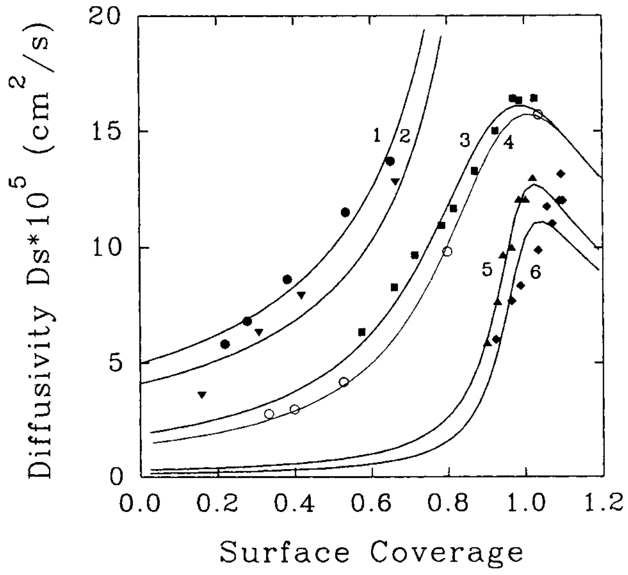

Figure 4. Surface diffusivities for CO_2/Carbolac carbon (1 & 2), CO_2/glass (3), CF_2Cl_2/Carbolac carbon (4) and NH_3/glass (5 & 6).

Symbols are experimental data. Curves are correlations by Eq. 28 (3-6) and Eq. 35 (1 & 2). Details are given in Table 1.

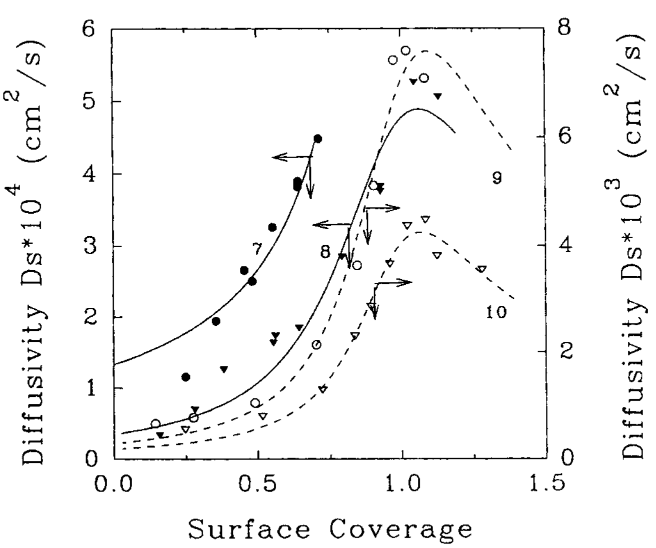

Figure 5. Surface diffusivities for C_3H_6/glass (7 & 8), C_4H_{10}/Carbon (9 & 10).

Symbols are experimental data. Curves are from Eq. 28 (8-10) and Eq. 35 (7). Details are given in Table 1.

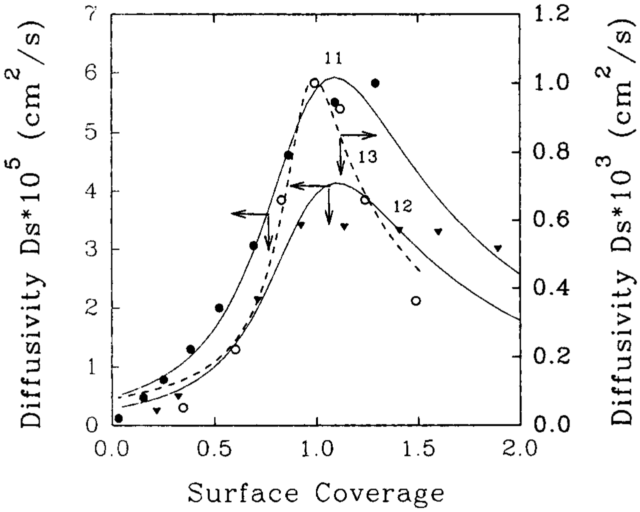

Figure 6. Surface diffusivities for Ar/silica (11 & 12) and N_2/carbon (17).

Symbols are experimental data and curves are correlations by Eq. 28. Details are given in Table 1.

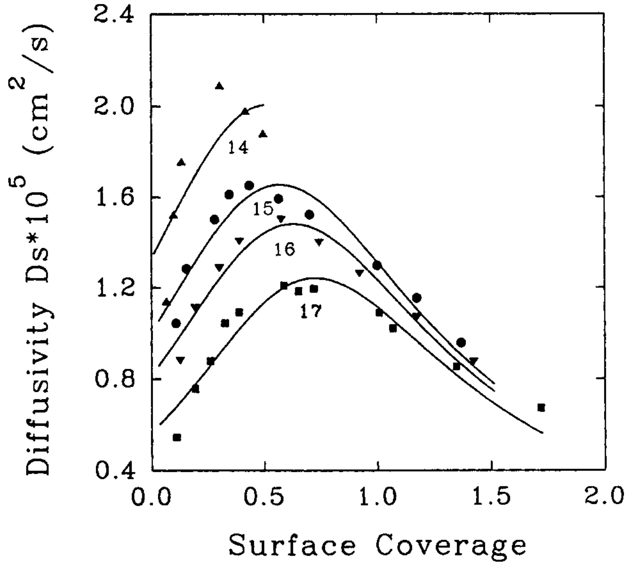

Figure 7. Surface diffusivities for C_6H_6/Aerosil.

Symbols are experimental data and curves are correlation by Eq. 28. Details are given in Table 1.

by H_1' and H_2', are also included in Table 2 for comparison. The values of the activation energy for surface diffusion are indeed approximately equal to or fractions of the heats of adsorption: $E_1 \approx H_1/m$ and $E_2 \approx H_2/m$. This result is in agreement with the empirical observation of Sladek et al. (1974), Eq. 34. The comparison between the heats of adsorption derived from the diffusivity data and the experimental results is not good, but reasonable.

Conclusion

A general model is derived for the concentration dependence of multilayer surface diffusivity based on the activated hopping mechanism. The model is valid for homogeneous surfaces. Multilayer surface diffusivity is expressed as a function of surface coverage and gas-solid interaction potential energy, which are imbedded in the parameter α. For monolayer surface diffusion, the equation is reduced to the HIO model. The model, in principle, requires no fitting parameters. It is also capable of predicting the maximum surface diffusivities as the surface concentration is varied. The activation energy for surface diffusion is approximately equal to or a fraction of the heat of adsorption.

Acknowledgment

This work was supported by the NSF under Grant CTS-8914754.

Notation

A = total surface area of the sorbent
b = Langmuir constant
c = BET constant
D = surface diffusivity
D_0 = surface diffusivity at zero surface coverage
E_1 = activation energy for surface diffusion on the first layer
E_2 = activation energy for surface diffusion on the second and high layers
H_1 = heat of adsorption on the first layer
H_2 = heat of adsorption on the second and high layers
H_1' = experimental heat of adsorption on the first layer
H_2' = experimental heat of adsorption on the second and high layers
J = flux
k_{ai} = rate constant of activation for surface diffusion from ith layer

Table 2. Activation Energies for Surface Diffusion and Heats of Adsorption

Sorbate	Sorbent	T °C	E_1 (kcal/mol)	E_2 (kcal/mol)	H_1* (kcal/mol)	H_2** (kcal/mol)	H'_1† (kcal/mol)	H'_2‡ (kcal/mol)
NH_3	Glass	40	8.37	5.10	9.73	5.58	>9.5	~6
NH_3	Glass	25	8.37	5.07	9.55	5.58	>9.5	~6
C_4H_{10}	Carbon	41.7	7.12	4.65	7.74	5.09	8.0	5.5
C_4H_{10}	Carbon	30	7.12	4.73	7.79	5.09	8.0	5.5
Ar	Silica	-184.1	0.62	0.076	2.10	1.56		
Ar	Silica	-195.6	0.62	0.122	2.06	1.56		
C_6H_6	Aerosil	51.8	4.78	4.41	7.72	7.35	11.5	8.5
C_6H_6	Aerosil	39.6	4.78	4.33	7.80	7.35	11.5	8.5
C_6H_6	Aerosil	30.2	4.78	4.25	7.89	7.35	11.5	8.5
C_6H_6	Aerosil	18.4	4.78	4.10	8.03	7.35	11.5	8.5

*Calculated from surface diffusivity data
**Heat of condensation
†Experimental value
‡Experimental value

k_{di} = rate constant of deactivation on the ith layer
m = empirical constant, 1, 2, or 3, defined by Eq. 34
M = rate of migration
n = number of multiadsorbed layers
q = amount adsorbed
q^v = amount of vacant sites
r = rate
S_i = surface area covered by i layers of adsorbed molecules
t = time
x = distance

Greek letters

α = gas-solid interaction parameter, Eq. 29
β = multilayer distribution parameter, Eqs. 6 and 32
δ = distance between adsorption sites
θ = fractional surface coverage based on an equivalent monolayer amount
μ = viscosity

Subscripts/superscripts

$*$ = activated adsorbate molecule
m = monolayer (equivalent) amount
v = vacant site

Literature Cited

Allen, M. P., and D. J. Tildesley, *Computer Simulation of Liquids*, Clarendon, Oxford (1988).

Arena, M. V., A. A. Deckert, and S. M. George, "Coverage-Dependent Surface Diffusion Expected from a Multiple-Site Hopping Model," *Surface Sci.*, **241**, 369 (1991).

Bowler, A. M., and E. S. Hood, "Time-Dependent Monte Carlo Studies of Surface Diffusion," *J. Chem. Phys.*, **94**, 5162 (1991).

Brunauer, S., P. H. Emmett, and E. Teller, "Adsorption of Gases in Multimolecular Layers," *J. Amer. Chem. Soc.*, **60**, 309 (1938).

Carman, P. C., and F. A. Raal, "Diffusion and Flow of Gases and Vapors Through Micropores: III. Surface Diffusion Coefficients and Activation Energies," *Proc. Roy. Soc.*, **A209**, 38 (1951).

Chen, Y. D., and R. T. Yang, "Concentration Dependence of Surface Diffusion and Zeolitic Diffusion," *AIChE J.*, **37**, 1579 (1991).

Chen, Y. D., and R. T. Yang, "Predicting Binary Fickian Diffusivities from Pure-component Fickian Diffusivities for Surface Diffusion," *Chem. Eng. Sci.*, **47**, 3895 (1992).

Ehrlich, G., and J. Stolt, "Surface Diffusion," *Annu. Rev. Phys. Chem.*, **31**, 603 (1980).

Frenkel, J., *Kinetic Theory of Liquids*, Dover Publication, New York (1955).

Friedrich, M., A. Seidel, and D. Gelbin, "Kinetics of Adsorption of Phenol and Indole from Aqueous Solutions on Activated Carbon," *Chem. Eng. Processes*, **24**, 33 (1989).

Gilliland, E. R., R. F. Baddour, G. P. Perkinson, and K. J. Sladek, "Diffusion on Surface: I. Effect of Concentration on the Diffusivity of Physically Adsorbed Gases," *Ind. Eng. Chem. Fundam.*, **13**, 95 (1974).

Gilliland, E. R., R. F. Baddour, and J. L. Russel, "Rate of Flow through Microporous Solids," *AIChE J.*, **4**, 90 (1958).

Haul, R. A. W., and B. Boddenberg, *The Porous Structure of Catalysts and Transport Processes in Heterogeneous Catalysts*, Akademiai Kiado, Budapest (1972).

Haul, R. A. W., and R. Peerbooms, "Oberflachendiffusion an EenergetischHomogenen und-Heterogenen Adsobentien," *Naturwiss.*, **45**, 109 (1958).

Higashi, K., H. Ito, and J. Oishi, "Surface Diffusion Phenomena in Gaseous Diffusion: I. Surface Diffusion of Pure Gas," *J. Atomic Energy Soc. Japan*, **5**, 846 (1963).

Hu, X., G. N. Rao, and D. D. Do, "Effect of Energy Distribution on Sorption Kinetics in Bidisperse Particles," *AIChE J.*, **39**, 249 (1993).

Itaya, A., Y. Fujita, N. Kato, and K. Okamoto, "Surface Diffusion Coefficient in Aqueous Phases Adsorption on Macroreticular Adsorbents," *J. Chem. Eng. Japan*, **20**, 638 (1987).

June, R. L., A. T. Bell, and D. N. Theodorou, "Molecular-Dynamics Study of Methane and Xenon in Silicalite," *J. Phys. Chem.*, **94**, 8232 (1990).

Kapoor, A., and R. T. Yang, "Contribution of Concentration Dependent Surface Diffusion to Rate of Adsorption," *Chem. Eng. Sci.*, **46**, 1995 (1991).

Kapoor, A., R. T. Yang, and C. Wong, "Surface Diffusion," *Catal. Rev.-Sci. & Eng.*, **31**, 129 (1989).

King, D. A., "Surface Diffusion of Adsorbed Species: A Review," *J. Vac. Sci. Technol.*, **17**, 241 (1980).

Komiyama, H., and J. M. Smith, "Surface Diffusion in Liquid-Filled Pores," *AIChE J.*, **20**, 1110 (1974).

Magda, J. J., M. Tirrell, and H. T. Davis, "Molecular-Dynamics of Narrow, Liquid-Filled Pores," *J. Chem. Phys.*, **83**, 1888 (1985).

Riekert, L., "Rates of Sorption and Diffusion on Hydrocarbons in Zeolites," *AIChE J.*, **17**, 446 (1971).

Robell, A. J., E. V. Ballou, and M. Boudart, "Surface Diffusion of Hydrogen on Carbon," *J. Phys. Chem.*, **68**, 2749 (1964).

Ross, J. W., and R. J. Good, "Adsorption and Surface Diffusion of *N*-Butane on Spheron 6 (2,700°C) Carbon Black," *J. Phys. Chem.*, **60**, 1167 (1956).

Roybal, L. A., and S. I. Sandler, "Surface Diffusion and Adsorbable Gases Through Porous Media," *AIChE J.*, **18**, 39 (1972).

Seidel, A., and P. S. Carl, "The Concentration Dependence of Surface Diffusion for Adsorption on Energetically Heterogeneous Adsorbents," *Chem. Eng. Sci.*, **44**, 189 (1989).

Sladek, K. J., E. R. Gilliland, and R. F. Baddour, "Diffusion on Surface: II. Correlation of Diffusivities of Physically and Chemically Adsorbed Species," *Ind. Eng. Chem. Fundam.*, **13**, 100 (1974).

Sudo, Y., D. M. Misic, and M. Suzuki, "Concentration Dependence of Effective Surface Diffusion Coefficient in Aqueous Phase Adsorption on Activated Carbon," *Chem. Eng. Sci.*, **33**, 1287 (1978).

Sun, L. M., and F. Meunier, "A Detailed Model for Non-isothermal Sorption in Porous Adsorbents," *Chem. Eng. Sci.*, **42**, 1585 (1987).

Suzuki, M., and T. Fujii, "Concentration Dependence of Surface Diffusion Coefficient of Propionic Acid in Activated Carbon Particles," *AIChE J.*, **28**, 380 (1982).

Tamon, H., M. Okazaki, and R. Toei, "Prediction of Surface Flow Coefficient of Adsorbed Gases on Porous Media," *AIChE J.*, **31**, 1226 (1985).

Worch, E., and R. Zapke, "Zur Kinetik der Adsorption von Phenolen an Aktivkohlen," *Chem. Tech.*, **37**, 375 (1985).

Yang, R. T., *Gas Separation by Adsorption Processes*, Butterworth, Boston (1987).

Yang, R. T., J. B. Fenn, and G. L. Haller, "Modification to the Higashi Model for Surface Diffusion," *AIChE J.*, **19**, 1052 (1973).

Yeh, Y. T., and R. T. Yang, "Diffusion in Zeolites with Mixed Cations," *AIChE J.*, **35**, 1659 (1989).

Manuscript received Apr. 2, 1992, and revision received Sept. 21, 1992.