

CONCENTRATION DEPENDENCE OF SURFACE DIFFUSIVITY OF NITROBENZENE AND BENZONITRILE IN LIQUID PHASE ADSORPTION ONTO AN ACTIVATED CARBON

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Key Words: Adsorption, Adsorption Kinetics, Intraparticle Diffusion, Surface Diffusion, Liquid Phase, Concentration Dependence, Activated Carbon, Mobility

Batch kinetic experiments were performed for adsorption of nitrobenzene and benzonitrile from aqueous solution onto activated carbon, the isotherms of which were only partially expressed by Freundlich equations. The experiments were carried out with adsorbents which had been equilibrated with a certain concentration of the solution in advance, to obtain adsorption rates representing certain ranges of the amount adsorbed. The intraparticle mass transfer rate was confirmed to be dominated by surface diffusion through the determination of pore diffusivity using a non-adsorptive substance, while the external mass transfer resistance could not be neglected. The surface diffusivities thus obtained were analyzed from the viewpoint of the non-ideality of the driving factor of surface diffusion, the amount adsorbed. Introduction of mobility of adsorbed molecule, derived through a treatment similar to ordinary diffusion in liquid phase, and assumption of the change of mobility with the energy of adsorption well explained the dependence of surface diffusivity in the whole range of concentration investigated.

Introduction

Adsorption processes in liquid phase, such as purification of wastewaters and concentration of dilute components in solutions, are often strongly affected by intraparticle diffusion since the intrinsic rate of adsorption at the adsorptive surface in the inside is rapid compared with that of diffusion. An understanding of the mechanism of intraparticle diffusion is hence necessary for the design of adsorption systems in liquid phase.

It has been pointed out that there exist two modes of mass transfer in porous adsorptive materials. One is the molecular diffusion mode within the pore volume and the other is the so-called surface diffusion mode, which is attributed to migration of adsorbed molecules on the interior surface of the adsorbent. An important feature of the latter is that the surface diffusivity D_s , which is naturally defined as a coefficient of mass flux driven by the gradient of amount adsorbed, is concentration-dependent.^{6-8,12,13,16,17)}

Since the surface diffusion often makes a large contribution to the intraparticle mass transfer, this dependency makes it complicated to treat the rate process in liquid-phase adsorption. However, the dependency itself could be a key to finding the basic mechanism of the surface diffusion phenomenon.

Although many previous studies have shown cases in which the surface diffusivity cannot be constant, the surface diffusivities obtained were so-called effective ones; namely, they were not local values with respect to the amount adsorbed. Only a few research results provide locally determined surface diffusivities vs. amount adsorbed.^{6,13)} The mechanism still remains unclear.

In this study, batch adsorption experiments were performed using adsorbents which had been equilibrated with certain liquid concentrations in advance, to obtain local values of surface diffusivity vs. concentration. The concentration dependence obtained was analyzed from the viewpoint of the thermodynamic non-ideality of the amount adsorbed.

1. Basic Equations

Suppose a stepwise small increase in liquid concentration is given to a batch system of adsorbent and liquid in an equilibrium condition of point A in Fig. 1. The system starts to change from point B towards a new equilibrium state of point C. The rate constant of this process is, then, a representative one for this concentration interval and hence can be a local value if the interval is small.

Considering both pore and surface diffusion for intraparticle mass transfer, the basic equation for a spherical adsorbent is:

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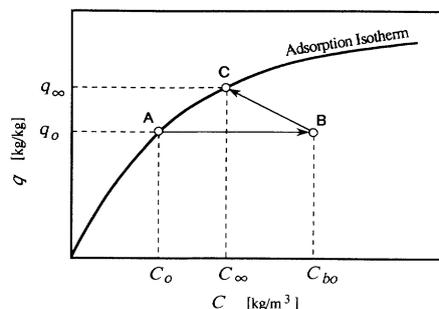


Fig. 1. Schematic figure of experimental process

$$\varepsilon \frac{\partial C}{\partial t} + \rho_{app} \frac{\partial q}{\partial t} = D_p \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C}{\partial r} \right) + \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \rho_{app} D_s \frac{\partial q}{\partial r} \right) \quad (1)$$

The following assumptions are made to simplify the equation:

- 1) The local equilibrium condition holds: $q = q(C)$
- 2) The surface diffusivity D_s and the slope of adsorption isotherm K are approximately constant for the concentration interval considered.

The first assumption is appropriate when the rate of intrinsic adsorption is rapid compared with that of diffusion, as is usually the case with physical adsorption. With the aid of the latter assumption the amount adsorbed, q , can be connected to the liquid concentration, C , by a linear relation within the concentration interval. Equation (1) then becomes

$$\frac{\partial C}{\partial t} = D_e \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C}{\partial r} \right) \quad (2)$$

where

$$D_e = \frac{(D_p + \rho_{app} K D_s)}{(\varepsilon + \rho_{app} K)} \quad (3)$$

Initial and boundary conditions for Eq. (2) are,

$$C = C_o \quad \text{at } t = 0 \quad (4)$$

$$C = \text{finite} \quad \text{at } r = 0 \quad (5)$$

$$(\varepsilon + \rho_{app} K) D_e \frac{\partial C}{\partial r} = k(C_b(t) - C) \quad \text{at } r = R \quad (6)$$

For the bulk liquid phase,

$$V \frac{dC_b}{dt} = -A_p (\varepsilon + \rho_{app} K) D_e \left[\frac{\partial C}{\partial r} \right]_{r=R} \quad (7)$$

$$C_b = C_{bo} \quad \text{at } t = 0 \quad (8)$$

Equations (2) and (7) with the above initial and boundary conditions are basically the same as those in Huang and Li³⁾ and can be solved by the method of Laplace transformation using the Heaviside expansion formula. The concentration of the bulk

liquid is derived to be

$$\frac{C_b - C_o}{C_{bo} - C_o} = \frac{\alpha}{\alpha + 1} + 6\alpha \sum_{n=1}^{\infty} \frac{\exp(-g_n^2 \tau)}{[9(\alpha + 1) + \alpha^2 g_n^2] - \alpha(\alpha + 6)g_n^2 \frac{1}{B_i} + \alpha^2 g_n^4 \frac{1}{B_i^2}} \quad (9)$$

where g_n 's are the positive roots of

$$\tan g_n = \frac{g_n(3B_i - \alpha g_n^2)}{3B_i + (B_i - 1)\alpha g_n^2} \quad (10)$$

and

$$\tau = \frac{D_e t}{R^2} \quad (11)$$

$$\alpha = \frac{3V}{A_p R (\varepsilon + \rho_{app} K)} \quad (12)$$

$$B_i = \frac{kR}{(\varepsilon + \rho_{app} K) D_e} \quad (13)$$

In the above equations, B_i represents the relative importance of the intraparticle mass transfer resistance to the film resistance. A large value of B_i means a small contribution by the film resistance. At the extreme of $B_i \rightarrow \infty$, therefore, the rate is controlled only by the intraparticle diffusion.

The effective diffusivity D_e , together with B_i , can be obtained by fitting Eq. (9) to the measured concentration-time curve.

Since D_e consists of the contributions of both surface diffusivity D_s and pore diffusivity D_p , one has to know the latter in advance to obtain D_s from D_e . Since pore diffusivity is related to molecular diffusivity D_{ab} by the parallel pore model as shown in Eq. (14), the structural parameter (ε/μ) of the adsorbent must be determined.

$$D_p = \left[\frac{\varepsilon}{\mu} \right] D_{ab} \quad (14)$$

To exclude the influence of surface diffusion, a non-adsorptive or relatively non-adsorptive compound should be used as a diffusing species in the kinetic experiments to obtain tortuosity. Details are described in the following sections.

2. Experimental

The adsorbent used was a commercial activated carbon, Takeda X-7000, whose shape was spherical. The physical properties are listed in Table 1. All adsorbent particles were washed with distilled water and evacuated at 110°C for 24 hours before experimental use. Nitrobenzene and benzonitrile of research grade provided by Wako Pure Chemicals

Table 1. Properties of the adsorbent

Shape		Spherical
Diameter	[m]	1.30×10^{-3}
Apparent density	[kg/m ³]	690
Porosity	[—]	0.65
Nitrogen surface area	[m ² /kg]	7.2×10^5

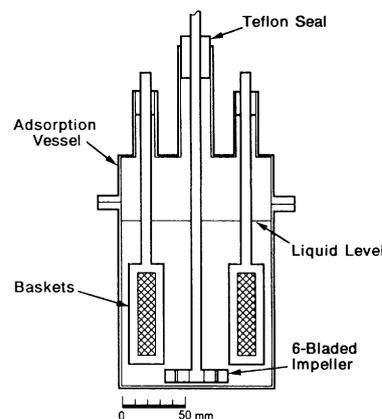
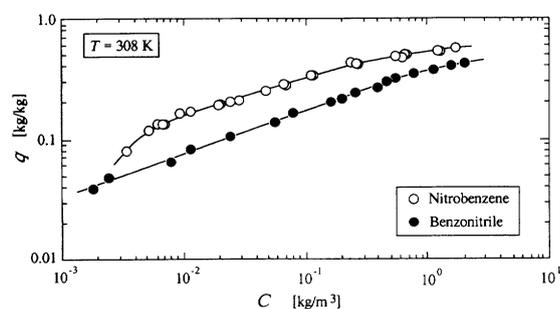
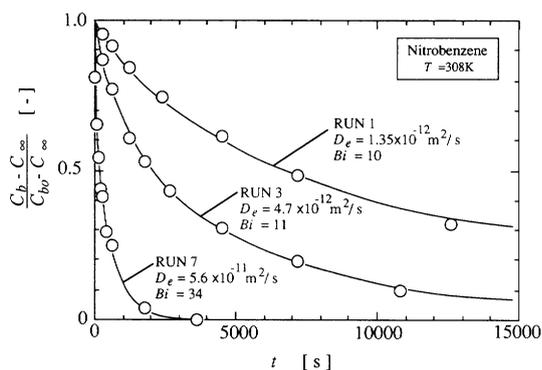
Inc. were used as adsorbate with no further purification.

The isotherms were determined by the conventional method: the adsorbent was added to 300 ml solution in an Erlenmeyer flask stopped by a Teflon-sealed screw cap, and was shaken in a thermostatted bath at 308 K. The equilibrium concentrations of nitrobenzene and benzonitrile were determined by an ultraviolet spectrophotometer (Shimadzu UV-260) at the wavelengths of 267 and 224 nm respectively.

A schematic sketch of the adsorber is shown in Fig. 2. A stirred tank (124 mm I.D.) made of Pyrex glass was equipped with two baffles (80 × 28 × 8 mm) made of 60 mesh stainless wire screen, which can hold the adsorbent inside. A six-bladed impeller (50 × 10 mm) made of stainless steel was rotated at about 1000 r.p.m. during the kinetic experiment.

A small amount of sieved adsorbent (14/16 mesh) was brought into contact with a solution to yield an equilibrium conditions of C_o and q_o , which is also a starting point in the kinetic experiment. The adsorbent baskets were lifted up temporarily from the solution and the liquid concentration was raised to C_{bo} . As a standard condition, C_{bo}/C_o was equal to about 1.5 while in the higher concentration range a ratio of 1.7 was needed to yield a reliable concentration-time relation. These ratios were still logarithmically small enough, compared with the whole concentration range investigated, to give local diffusivities. At $t=0$ in the kinetic experiment the adsorbent basket was suddenly immersed in the agitated solution. A stepwise increase in liquid concentration was achieved by this procedure. Measurements were made by taking small samples from the solution at planned intervals and monitoring the concentration with a spectrophotometer.

For the determination of the pore diffusivity D_p , glucose, the adsorbed amount of which was confirmed to be negligibly small compared with those of nitrobenzene and benzonitrile, was used as a diffusing species. The kinetic experiments in this system were performed by almost the same procedure as that for the surface diffusion measurement except that the bulk initial concentration was zero; that is, desorption runs were adopted in this system. Concentrations were measured by a total organic carbon analyzer (Shimadzu TOC-10A).

**Fig. 2.** Schematic sketch of adsorber**Fig. 3.** Adsorption isotherms of nitrobenzene and benzonitrile**Fig. 4.** Batch kinetic experiments for nitrobenzene

3. Results and Discussion

3.1 Isotherms

The isotherms of nitrobenzene and benzonitrile measured at 308 K are shown in Fig. 3. Though both isotherms have straight portions, an incipient shift to Henry's law in the lower concentration range for nitrobenzene and asymptotic behavior to saturation in the higher concentration range for both adsorbates are recognized. As a result, the Freundlich equation can only partly express the isotherms of the systems studied.

3.2 Effective diffusivity

Some results of the kinetic experiments are illustrated in Fig. 4 together with fitted curves by Eq.

(9). The curves agree fairly well with the experimental points. The agreements were similar in all the experiments, which confirmed the validity of the assumptions adopted in this study. The effective diffusivity thus obtained increased significantly with concentration.

It should be noted that the Biot numbers fall into finite values rather than infinity. This means that the external mass transfer resistance cannot be neglected in this system, even under such an intensive mixing condition as mentioned above. A considerable increase in the intraparticle mass transfer rate by surface diffusion is thus expected in this system. The external mass transfer coefficients were calculated by Eq. (13) to be around 2×10^{-4} m/s, which was roughly equivalent to the Sherwood number of 200. Similar values have been reported by Muraki *et al.*⁸⁾, where almost the same type of adsorber was used, and also in several studies^{7,9,14)} where adsorbents were held by impellers instead of baffles.

3.3 Pore diffusivity

It is often the case that intraparticle mass transfer is controlled by surface diffusion in the physical adsorption in liquid phase. It was confirmed that this was the situation in the system studied. The results are described briefly below.

In some preliminary experiments on the adsorption equilibrium of glucose solution, the amount adsorbed was confirmed to be so small that a negligible contribution of surface diffusion could be assumed. However, the amount itself could not be neglected in comparison with that held in the pore volume. The effective diffusivity for this system is thus expressed as follows:

$$D_e = \frac{D_p}{(\varepsilon + \rho_{app}K)} \quad (15)$$

The denominator of the above equation can be determined by a mass balance between the initial and final conditions of the kinetic experiment as done by Komiyama and Smith.⁵⁾

$$\varepsilon + \rho_{app}K = \frac{\rho_{app}V}{W} \frac{C_\infty}{C_o - C_\infty} \quad (16)$$

Figure 5 shows the result of a kinetic experiment for glucose. The fitted curve of Eq. (9) agrees well with the data. Note that the Biot number must have an infinitely large value to get the best fit here, in contrast to those of the adsorptive compounds. The intensity of the mixing surely achieved negligible mass transfer resistance outside the particle when the pore diffusion was controlling inside the particle.

The structural parameter obtained is as follows:

$$(\varepsilon/\mu) = 0.078$$

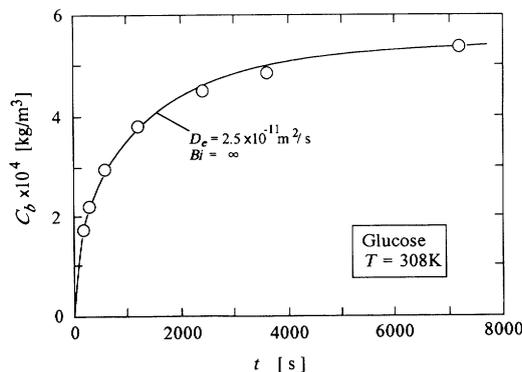


Fig. 5. Desorption experiment for glucose

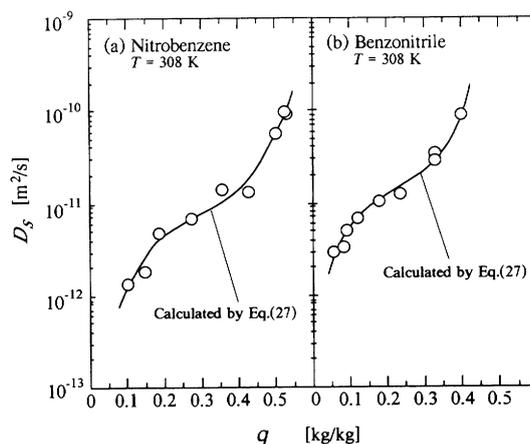


Fig. 6. Relation between surface diffusivity and amount adsorbed (a) for nitrobenzene and (b) for benzointrile

Though the tortuosity itself need not be determined, its calculation was attempted to obtain $\mu = 4.0$ using macro-porosity in ε term according to the recommendation by Kawazoe *et al.*⁴⁾ This value is consistent with other research results obtained so far for activated carbons, such as those of Kawazoe *et al.*⁴⁾

D_p 's for the nitrobenzene system and benzointrile system were calculated by Eq. (14). It was confirmed that the pore diffusion contributed only a few percent of the total mass flux in almost all of the experiments. Hence, the surface diffusivity can be approximated by the effective diffusivity in the systems of adsorptive compounds studied.

3.4 Concentration dependence of surface diffusivity

Surface diffusivities are plotted against the amount adsorbed in Fig. 6. They vary almost a hundredfold with the amount adsorbed. Such significant concentration dependency as a variation of almost two orders of magnitude is first confirmed by the authors experimentally in liquid-phase adsorption in the present study. They seem empirically to be correlated by an exponential function. However, this type of function has little theoretical basis for the isotherms of the systems studied here. In addition, the data

seem to have a sigmoid form rather than to be exponentially linear.

A correlation of D_s by a power function formula of q has been proposed for Freundlich isotherms,^{8,13} based on a similar concept proposed by Gilliland *et al.*²⁾ for gaseous phase adsorption. The activation energy of surface diffusion is assumed to vary linearly with the heat of adsorption. This assumption leads to Eq. (17).

$$D_s = D_s^*(q/q^*)^{(a/n)} \quad (17)$$

This formula might be applicable to the middle concentration range of nitrobenzene and the major part of the concentration range of benzonitrile, where the isotherms were relatively straight, to prove the partial applicability of Freundlich equations. However, the power function is obviously not suitable for the whole range of the dependency obtained here, because the power function should be convex to the abscissa in Fig. 6 whereas the data show sigmoidal changes.

In ordinary diffusion in liquid phase, concentration dependence of the diffusivity is often caused by the nonlinearity of liquid concentration against activity. The amount adsorbed, q , is thought to be typical of nonlinear factors. The surface diffusivity, which is defined with the nonlinear quantity, must be affected by the nonlinearity. Introducing *mobility of adsorbed molecule* by a similar concept to ordinary liquid-phase diffusion, we can examine the effect of nonlinearity as follows.

Consider adsorbed molecules subjected to a gradient of the amount adsorbed. The chemical potential of adsorbed phase at a point $z=z$ can be expressed by a liquid-phase activity which can be in equilibrium with the amount adsorbed at z . Accordingly, the force acting on an adsorbed molecules is expressed as

$$\begin{aligned} F &= -\frac{1}{N_A} \cdot \frac{\partial \mu_a}{\partial z} \\ &= -\frac{1}{N_A} \cdot \frac{\partial \mu_i(C)}{\partial z} \\ &= -k_B T \frac{\partial \ln a_i}{\partial z} \end{aligned} \quad (18)$$

Denoting the mobility of an adsorbed molecule as u_a , the average velocity of adsorbed molecules is

$$v_a = u_a \cdot F \quad (19)$$

Since the amount adsorbed per unit volume is the product of ρ_{app} and q , the mass flux of adsorbed molecules is given by

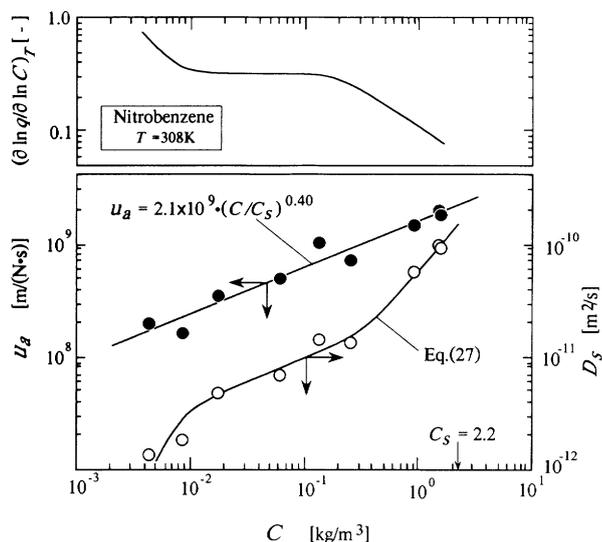


Fig. 7. Correlation of mobility and surface diffusivity with liquid concentration for nitrobenzene

$$\begin{aligned} J_s &= \rho_{app} q v_a \\ &= -\rho_{app} q u_a k_B T \frac{\partial \ln a_i}{\partial z} \end{aligned} \quad (20)$$

On the other hand, the definition of the surface diffusivity is

$$J_s = -\rho_{app} D_s \frac{dq}{dz} \quad (21)$$

which is compared with Eq. (20) to yield

$$D_s = k_B T u_a \left(\frac{\partial \ln a_i}{\partial \ln q} \right)_T \quad (22)$$

The activity of adsorbate in solution could be substituted by the liquid-phase concentration provided linearity between them holds—for example, under ideal dilute solution approximation which is the case in this study.

$$D_s = k_B T u_a \left(\frac{\partial \ln C}{\partial \ln q} \right)_T \quad (23)$$

This result shows that we need not take the nonlinearity effect into account in discussing the concentration dependence provided that the Freundlich isotherm holds. For other isotherms, however, the introduction of u_a enables us to discuss the mass transfer rate more precisely.

The D_s data can be converted to u_a data with the aid of the information from isotherms, namely the logarithmic slopes of the adsorption isotherms which are shown in Figs. 7 and 8. In the middle concentration range of nitrobenzene and in the major concentration range of benzonitrile the slope shows almost constant value, which corresponds to the straight portion in Fig. 3.

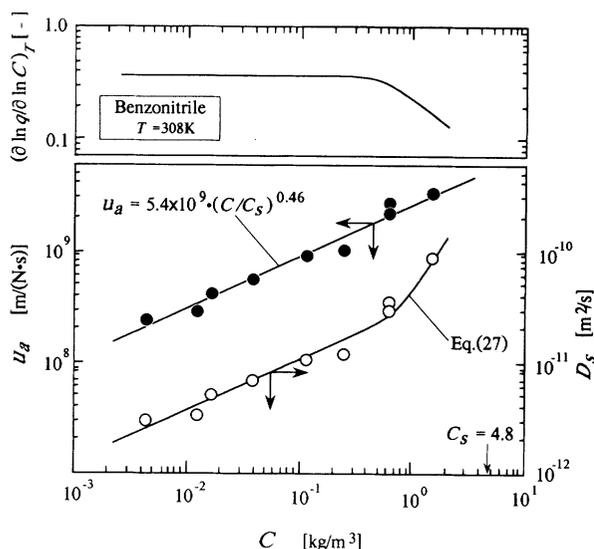


Fig. 8. Correlation of mobility and surface diffusivity with liquid concentration for benzonitrile

The obtained u_a 's are plotted against C also in Figs. 7 and 8 together with the D_s data for reference. For each system, the u_a 's seem to be correlated by a straight line with slope of 0.4–0.5 as expressed by the correlation equations in the figures. Though we have to admit relatively large uncertainties in the logarithmic slope of the isotherm, the linearity obtained is quite promising.

This linearity could be interpreted as follows. Let us assume an Arrhenius-type expression for the mass transfer property u_a .

$$u_a = k_o \exp\left(-\frac{\Delta E_a}{RT}\right) \quad (24)$$

It is acceptable to set a linear relation between the activation energy and adsorptive energy as done by Gilliland *et al.*,²⁾ Suzuki and Fujii¹³⁾ and Muraki *et al.*⁸⁾ For adsorbate with small solubility, the isosteric heat of adsorption may be approximated by the sum of the adsorption potential and the heat of dissolution as derived by Urano *et al.*¹⁵⁾ Though Urano *et al.* showed this relation only for the Freundlich isotherm, the relation should be true for any type of isotherm as long as we accept the theory of adsorption on heterogeneous surfaces proposed by Roginsky¹⁰⁾ and take the saturation concentration, C_s , for the standard concentration of energy term as explained by Seidel and Carl.¹¹⁾

$$q_{st} = RT \ln(C_s/C) + \Delta H_{sol} \quad (25)$$

A linear, not necessarily proportional, relation between ΔE_a and q_{st} is sufficient to yield the power function formula at a certain temperature.

$$u_a = u_{ao} \left(\frac{C}{C_s}\right)^a \quad (26)$$

Combining with Eq. (23),

$$D_s = k_B T u_{ao} \left(\frac{\partial \ln C}{\partial \ln q}\right)_T \left(\frac{C}{C_s}\right)^a \quad (27)$$

where a is the coefficient of linear expression of ΔE_a with q_{st} . Equation (27) is considered to be a general form of Eq. (17) since it reduces to Eq. (17) if the Freundlich isotherm holds.

Note that the mobility used here is distinguished from the reciprocal of resistance coefficient derived by Gilliland *et al.*¹⁾ The trial of their correlation was not successful.

Figures 7 and 8 show that a is around 0.4–0.5 for these aromatic compounds. This result is in line with those obtained by Muraki *et al.*⁸⁾ for three kinds of aromatic compounds with Freundlich isotherms, where the concentration–time curves of kinetic experiments using virgin carbons were analyzed numerically using Eq. (17) for surface diffusivity.

Using the correlation equations of the mobilities, Eq. (27) gives the calculated surface diffusivity as shown by the solid lines in Figs. 7 and 8. They are also shown against q in Fig. 6 with the aid of isotherm relations. The calculated curves well correlate the D_s data in the whole range of the concentration investigated. The sigmoid change in Fig. 6 can now be understood as follows. While the logarithmic slope is constant over a certain range of concentration, Eq. (27) reduces to a simple power function of q , as stated above, to yield a convex portion. The decrease in logarithmic slope in the higher concentration range as shown in Figs. 7 and 8 results both in the rise in D_s against C as seen in the figures, and in the quite small change of q against C as shown by isotherms, thus yielding a steep rise in D_s – q plots in Fig. 6. As a result, the plot of D_s against q shows a sigmoid form rather than a convex or exponentially linear one.

As explained, the logarithmic linearity between u_a and C implies change in mobility caused by change in adsorptive energy. However, the theoretical basis for the connection of the diffusivity or mobility with temperature remains unclear. Consideration of the basic mechanism of surface diffusion would be desirable to solve this problem.

Conclusion

Local values of surface diffusivities were determined through batch kinetic experiments in limited ranges of amount adsorbed. Pore diffusion was confirmed to make a negligible contribution to intraparticle mass transfer through kinetic experiments using a relatively non-adsorptive substance as diffusing species, while the film resistance could not be neglected.

Introduction of *mobility of adsorbed molecule* and assumption of change in mobility with energy of adsorption well correlated the surface diffusivity obtained with amount adsorbed in the whole range of concentration investigated.

Acknowledgment

The authors are indebted to Messrs. Minoru Murata and Hidehiko Kashiya for their assistance in the experimental work.

Nomenclature

A_p	= particle surface area	[m ²]
a	= coefficient of linear expression of ΔE_a with q_{st}	[—]
a_i	= activity	[—]
B_i	= Biot number	[—]
C	= concentration	[kg/m ³]
D_{ab}	= molecular diffusivity	[m ² /s]
D_e	= effective diffusivity	[m ² /s]
D_p	= pore diffusivity	[m ² /s]
D_s	= surface diffusivity	[m ² /s]
D_s^*	= surface diffusivity at $q=q^*$	[m ² /s]
ΔE_a	= activation energy for mobility	[J/mol]
F	= force acting on adsorbed molecules	[N]
g_n	= roots of Eq. (10)	[—]
ΔH_{sol}	= heat of dissolution	[J/mol]
J_s	= mass flux of adsorbed molecules	[kg/(m ² ·s)]
K	= dq/dC ; slope of adsorption isotherm	[m ³ /kg]
k	= external mass transfer coefficient	[m/s]
k_B	= Boltzmann constant	[J/K]
k_o	= pre-exponential factor for mobility	[m/(N·s)]
N_A	= Avogadro's number	[1/mol]
n	= reciprocal exponent of Freundlich isotherm	[—]
q	= amount adsorbed	[kg/kg]
q^*	= standard amount adsorbed in Eq. (17)	[kg/kg]
q_{st}	= isosteric heat of adsorption	[J/mol]
R	= radius of adsorbent particle	[m]
r	= radial coordinate	[m]
T	= temperature	[K]
t	= time	[s]
u_a	= mobility of adsorbed molecules	[m/(N·s)]
u_{ao}	= constant defined by Eq. (26)	[m/(N·s)]
V	= volume of bulk liquid	[m ³]
v_a	= average velocity of adsorbed molecules	[m/s]
W	= adsorbent dosage	[kg]
z	= distance coordinate	[m]

α	= constant given by Eq. (12)	[—]
ε	= porosity of adsorbent	[—]
μ	= tortuosity factor	[—]
μ_a	= chemical potential in adsorbed state	[J/mol]
μ_l	= chemical potential in solution	[J/mol]
ρ_{app}	= apparent density of adsorbent	[kg/m ³]
τ	= dimensionless time	[—]

<Subscripts>

b	= bulk liquid
bo	= initial condition of bulk liquid
o	= pertaining to point A in Fig. 1
∞	= pertaining to point C in Fig. 1

Literature Cited

- Gilliland, E. R., R. F. Baddour and J. L. Russell: *AIChE J.*, **4**, 90 (1958).
- Gilliland, E. R., R. F. Baddour, G. P. Pekinson and K. J. Sladek: *Ind. Eng. Chem. Fundam.*, **13**, 95 (1974).
- Huang, T. C. and K. Y. Li: *Ind. Eng. Chem. Fundam.*, **12**, 50 (1973).
- Kawazoe, K., I. Sugiyama and Y. Fukuda: *Kagaku Kogaku*, **30**, 1007 (1966).
- Komiyama, H. and J. M. Smith: *AIChE J.*, **20**, 728 (1974).
- Miura, K., K. Hashimoto and S. Nagata: *Preprint of the 40th Annual Meeting of Soc. Chem. Eng. Japan*, E311 (1975).
- Moon, H. and W. K. Lee: *Colloid Interface Sci.*, **96**, 162 (1983).
- Muraki, M., Iwashima and T. Hayakawa: *J. Chem. Eng. Japan*, **15**, 34 (1982).
- Peel, R. G., A. Benedek and C. M. Crowe: *AIChE J.*, **27**, 26 (1981).
- Roginsky, S. Z.: "Adsorption and Catalysis on Non-Uniform Surface," USSR Academy (1949).
- Seidel, A. and P. S. Carl: *Chem. Eng. Sci.*, **44**, 189 (1989).
- Sudo, Y., D. M. Misic and M. Suzuki: *Chem. Eng. Sci.*, **33**, 1287 (1978).
- Suzuki, M. and T. Fujii: *AIChE J.*, **28**, 380 (1982).
- Suzuki, M. and K. Kawazoe: *J. Chem. Eng. Japan*, **8**, 79 (1975).
- Urano, K., Y. Koichi and Y. Nakazawa: *J. Colloid Interface Sci.*, **81**, 477 (1981).
- Watanabe, F. and M. Hasatani: *Kagaku Kogaku Ronbunshu*, **8**, 685 (1982).
- Watanabe, F. and M. Hasatani: *Kagaku Kogaku Ronbunshu*, **10**, 461 (1984).

(Presented in part at the 21st Autumn Meeting of The Soc. of Chem. Engrs., Japan at Fukuoka, October, 1988)