Model for Surface Diffusion in Liquid-Phase Adsorption

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Based on the absolute-rate theory, a consistent interpretation was provided for the dependence of surface-diffusion coefficient, D_s, on temperature and the amount adsorbed in various liquid-phase adsorption systems, such as the Langmuir-, Freundlich- and Jossens-type adsorption. It was demonstrated that a restricted molecular diffusion model for surface diffusion was useful for the analysis of the characteristic features of D_s. A formulation of D_s was derived based on the model and was applied to the analysis of surface-diffusion phenomena in various adsorption systems. The temperature dependence could be interpreted by assuming surface diffusion as an activated process. By taking into account the change in both the logarithmic slope of an adsorption isotherm and an adsorption potential, the concentration dependence of D_s could be interpreted irrespective of the type of the adsorption isotherms.

Introduction

It is well known that surface diffusion has an extremely important role for intraparticle diffusion in many cases of both gas- and liquid-phase adsorption systems. A number of studies on surface diffusion have been carried out to elucidate the mechanism of surface diffusion, and to develop an estimation procedure of surface-diffusion coefficient, D_s. The estimation of D_s, however, is extremely difficult because D_s varies to a high degree according to the combination of adsorbates, adsorbents, and solvents. Strict understanding of the surface-diffusion mechanism is essential for the establishment of the estimation procedure of D_s. In earlier studies, the dependence of D_s on both temperature and the amount adsorbed, q, was investigated as characteristic features of surface diffusion. On the basis of the studies from the standpoint of the temperature and concentration dependence of D_s, the migration mechanism of adsorbate molecules on the surface of adsorbents has been discussed (Kapoor et al., 1989; Suzuki, 1990).

In both gas- and liquid-phase adsorption systems, the temperature dependence of D_s has been conventionally interpreted by the Arrhenius-type equation. On the other hand, the dependence of D_s on q has been frequently discussed in connection with a change in the heat of adsorption. In gaseous systems, Gilliland et al. (1974) correlated activation energies of surface diffusion, E_s, with the heats of adsorption by introducing a proportional coefficient, α'. They indicated that the concentration dependence of D_s was attributed to the change in the heat of adsorption due to the change in q. Sladek et al. (1974) rearranged many experimental results in a wide range from physisorption to chemisorption by a single straight correlation on the basis of this concept.

In liquid-phase adsorption, the variation of D_s has been explained by considering the change in an adsorption energy. Komiyama and Smith (1974a,b) studied surface diffusion of benzaldehyde in liquid-filled pores of Amberlite (polystyrene) particles by using methanol/water mixtures of various compositions as a solvent. It was demonstrated that an increase in methanol content in the mixtures brought about a decrease in adsorption capacity and an increase in D_s. The results were interpreted in terms of a two-step theory for surface migration based on the Eyring's rate theory. The two-step theory deals with surface diffusion by considering two conceptual processes. One is the formation of a hole on the surface and the other is the migration of an adsorbate molecule into the hole. The value of E_s is also divided into two contributions. One is due to the hole-making step and the other to the breaking of the bond between the adsorbate molecules and the surface. It was also suggested that the contribution of the bond breaking was approximated as a certain fraction of the heat of adsorption. Sudo et al. (1978) interpreted concentration dependence of D_s by applying a function of a final amount adsorbed. Suzuki and Fujii (1982) studied aqueous

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adsorption of propionic acid onto an activated carbon. Strict determination of adsorption characteristics was made from the viewpoints of adsorption equilibrium, mass-transfer rates, and thermodynamic properties. It was reported that an adsorption isotherm could be represented by the Freundlich equation, and that D_s increased with an increase in q. The strong concentration dependence of D_s was explained by taking into account the change in the heat of adsorption due to the change in the surface coverage of propionic acid. Itaya et al. (1987) determined D_s in the aqueous adsorption of phenol derivatives onto macroreticular (Amberlite) resins by finite-bath adsorption experiments. The linear correlation between E_s and an isosteric heat of adsorption, Q_{st}, was indicated by analyzing the concentration dependence of D_s. By applying the concept of molecular diffusion to the surface diffusion, they suggested that the slope and intercept of the linear relation corresponded to the contributions of a jumping (bond-breaking) step and a hole-making step, respectively. It was also reported that the ratio of the contribution of the jumping step to $(-Q_{st})$ ranged from about 0.4 to 0.6. The results were in accord with the consideration of Komiyama and Smith (1974a,b). Muraki et al. (1982) also studied the dependence of D_s on q by a finite-bath aqueous adsorption of benzene derivatives onto an activated carbon. It was reported that the ratio of E_s to an adsorption energy was almost equal to 0.5 even in liquid-phase adsorption. Moon and Lee (1983) investigated a liquid-phase adsorption of phenols with an activated carbon in a batch adsorber. An attempt was made to explain the concentration dependence of D_s by a simple empirical equation of the time and particle-volume average value of q. Miyahara and Okazaki (1992, 1993) showed a significant concentration dependence of D_s of benzene derivatives in an aqueous adsorption by batch kinetic experiments. They attempted to explain the concentration dependence of D_s by applying the Eyring's rate theory. Similarly, in the previous studies (Komiyama and Smith, 1974b; Itaya et al., 1987), E_s was assumed to consist of two contributions due to a hole-making step and a jumping one. They considered that a rate-controlling step was the hole-making step under a potential field of adsorption. The value of E_s was assumed to be a certain fraction of the sum of the evaporative energy, ΔE_v, of an adsorbate and the adsorption potential, E_{ap}. The influence of both concentration and temperature on D_s in the aqueous adsorption of the benzene derivatives onto an activated carbon was quantitatively interpreted on the basis of the concept. In previous articles (Miyabe and Suzuki, 1992, 1993a,b, 1994a,b, 1995), the authors studied adsorption phenomena in reversed-phase liquid chromatography (RP-LC) from kinetic and thermodynamic points of view as well as adsorption equilibrium. An adsorption isotherm was expressed by the Langmuir equation. The significance of surface diffusion was confirmed for the intraparticle diffusion of adsorbate molecules in RP packing materials in both gas- and liquid-phase adsorption systems. It was reported that a positive concentration dependence of D_s could be interpreted by considering a chemical-potential driving force. In a recent article (Miyabe and Takeuchi, 1997), the authors proposed a restricted molecular-diffusion model as one model for the surface-diffusion mechanism. A formulation of D_s was derived on the basis of the absolute-rate theory. Similar to the previous studies (Komiyama and Smith, 1974b; Itaya et al., 1987; Miyahara and Okazaki, 1992, 1993), the surface diffusion mechanism was assumed to consist of two hypothetical processes, that is, a hole-making process and a bond-breaking one. An activation energy of the hole-making process was correlated with ΔE_v of a solvent, not of an adsorbate, and that of the bond-breaking process was assumed to be equal to a certain fraction of $(-Q_{st})$. The validity of the restricted molecular-diffusion model was demonstrated through analyses of various experimental data in liquid-phase adsorption. In liquid-phase adsorption, the ratio of $E_s/(-Q_{st})$ larger than unity has been frequently reported. On the other hand, smaller values of E_s in comparison with $(-Q_{st})$ were sometimes observed even in liquid-phase adsorption. A quantitative explanation could be provided for the various situations relating to the ratio of $E_s/(-Q_{st})$ in liquid-phase adsorption by the restricted molecular-diffusion model for surface diffusion (Miyabe and Takeuchi, 1997).

This article is concerned with a quantitative analysis of the dependence of D_s on various factors, that is, temperature, the amount adsorbed, and the adsorptive interaction between adsorbate molecules and the surface of adsorbents, on the basis of the restricted molecular-diffusion model. Previously published surface-diffusion data in liquid-phase adsorption were analyzed by applying the model. First, the model was applied to the analysis of surface diffusion data in RP-LC (Miyabe and Suzuki, 1992), in which an adsorption isotherm could be represented by the Langmuir equation. Then the dependence of D_s on both temperature and the amount adsorbed in different types of liquid-phase adsorption other than the Langmuir-type, that is, the Freundlich- (Suzuki and Fujii, 1982) and the Jossens- (Itaya et al., 1987) type systems, was quantitatively analyzed. Irrespective of the type of adsorption systems, the temperature dependence of D_s could be interpreted by using the Arrhenius-type equation. On the other hand, the concentration dependence of D_s could be interpreted by taking into account the variation of both the logarithmic slope of an adsorption isotherm, $(d \ln c/d \ln q)$, and E_{ap}. The change in both factors resulted from the change in q. It was confirmed that the change in E_{ap} due to the change in q was equal to that of Q_{st}. The various characteristic features of surface diffusion could be consistently interpreted on the basis of the restricted molecular diffusion model.

Theory

The temperature dependence of D_s has usually been represented by the Arrhenius equation on the assumption that surface diffusion is an activated process:

$$D_s = D_{s0} \exp(-E_s/R_g T). \tag{1}$$

The value of E_s has been conventionally approximated as a certain fraction of $(-Q_{st})$ (Gilliland et al., 1994):

$$E_s = \alpha'(-Q_{st}). \tag{2}$$

By substituting Eq. 2 into Eq. 1, the following ordinary equation is derived:

$$D_s = D_{s0} \exp[-\alpha'(-Q_{st})/R_g T]. \tag{3}$$

Similarly, molecular diffusion in liquid phase is regarded as an activated process:

$$D_m = D_{m0} \exp(-E_m/R_g T). \qquad (4)$$

Another formula of molecular diffusivity, D_m, was derived on the basis of the absolute-rate theory (Glasstone et al., 1964). From the definition of diffusion coefficient, D_m is expressed as follows:

$$D_m = \lambda^2 \tau, \qquad (5)$$

where λ is the distance between neighboring equilibrium positions and τ is a rate constant. According to the theory, τ is represented by assuming that a transmission coefficient is unity:

$$\tau = (kT/h)(F^{\ddagger}/F)\exp(-E_m/R_g T), \qquad (6)$$

where F and $F^{\ddagger}$ are partition functions for initial and activated states, respectively. The following equation is obtained by assuming that $F^{\ddagger}$ does not contain only the contribution due to the translation in the direction of the mass transfer in comparison with F:

$$F^{\ddagger}/F = (2\pi mkT)^{1/2} v_f^{1/3}/h. \qquad (7)$$

If a hole-making in a solvent is required for a molecular diffusion, the activation energy of the migration process should be correlated with the energy of evaporation:

$$E_m = \alpha \Delta E_v. \qquad (8)$$

By combining Eqs. 5–8, D_m is formulated as follows:

$$D_m = \left(\lambda^2/v_f^{1/3}\right)(kT/2\pi m)^{1/2} \exp(-\alpha \Delta E_v/R_g T) \qquad (9)$$

$$v_f^{1/3} = (V/N_A)^{1/3}(CR_g T/\Delta E_v). \qquad (10)$$

By comparing Eqs. 4 and 9, the following relationships should be observed:

$$D_{m0} = \left(\lambda^2/v_f^{1/3}\right)(kT/2\pi m)^{1/2} \qquad (11)$$

$$E_m = \alpha \Delta E_v. \qquad (12)$$

In a recent article (Miyabe and Takeuchi, 1997), it was indicated that D_s was probably equal to D_m under limited conditions in which the adsorptive interaction between adsorbate molecules and the surface of adsorbents was negligibly small. Because the intensity of the adsorptive interaction is usually represented by Q_{st}, the situation that the adsorptive interaction is negligible corresponds to $Q_{st} = 0$. On the basis of the conventional concept of surface diffusion, D_s is calculated to be equal to D_{s0} according to Eq. 3 in such a case. In a number of studies relating to liquid-phase adsorption (Awum et al., 1988; Komiyama and Smith, 1974a; Ma et al., 1988; Miyabe and Suzuki, 1992, 1993b, 1994a,b, 1995; Suzuki and Fujii, 1982; Suzuki and Kawazoe, 1975), experimental values of D_{s0} have been reported ranging from about 10^{-4} cm$^2 \cdot$s^{-1}to 10^{-1} cm$^2 \cdot$s^{-1}, which are larger than D_m. The value of D_m is approximated to be of the order of 10^{-5} cm$^2 \cdot$s^{-1} by various estimation procedures such as the Wilke–Chang equation (Reid et al., 1987; Treybal, 1980). It may be unreasonable that D_s is several orders of magnitude larger than D_m, even though it's under the conditions that the adsorptive interaction is almost negligible. A different formulation of D_s should be derived on the basis of D_m.

In previous papers (Itaya et al., 1987; Komiyama and Smith, 1974b), it was suggested that E_s consisted of the contribution of a hole-making process, E_h, and that of a bond-breaking (jumping) one, E_b, as indicated in Eq. 13.

$$E_s = E_h + E_b. \qquad (13)$$

It was also suggested that the contribution of the jumping process was correlated with Q_{st}. A linear correlation between E_s and Q_{st} was proposed (Itaya et al., 1987; Komiyama and Smith, 1974b):

$$E_s = E_h + \beta(-Q_{st}). \qquad (14)$$

The first and second terms on the righthand side of Eq. 14 represent the contributions due to the hole-making process and the jumping process, respectively. In a recent article (Miyabe and Takeuchi, 1997), the authors suggested that surface diffusion was regarded as a molecular diffusion restricted due to the adsorptive interaction. By applying the absolute rate theory to the concept, the meaning of E_s was considered. Similar to the previous concept (Itaya et al., 1987; Komiyama and Smith, 1974b), E_s was assumed to be divided into two contributions. One is the contribution due to a hole-making process in a solvent phase in the neighborhood of the surface of an adsorbent. The generation of the hole is assumed to be achieved by the removal of solvent molecules, not of adsorbate molecules, in a potential field of adsorption. An adsorbate molecule presented at a neighbor adsorption site may transfer into the hole. The activation energy of the hole-making process is probably correlated with ΔE_v of the solvent, not of the adsorbate. The other is the contribution due to a jumping process of the adsorbate molecules. The transfer of the adsorbate molecules into the next hole is assumed to be attained by the gain of a certain amount of activation energy, which is required for breaking the adsorptive interactions between the adsorbate molecules and the surface of an adsorbent. The activation energy of the jumping process of the adsorbate should be correlated with Q_{st}. On the basis of these considerations, Eq. 14 can be represented as follows:

$$E_s = \alpha \Delta E_v + \beta(-Q_{st}). \qquad (15)$$

By taking into account the experimental result that D_s is probably equal to D_m at $Q_{st} = 0$ (Miyabe and Takeuchi, 1997), the first term in Eq. 15 seems to be identical to E_m as Eq. 12:

$$E_s = E_m + \beta(-Q_{st}). \qquad (16)$$

The activation energy of molecular diffusion, E_m, can be converted to E_s by the addition of the contribution due to the adsorptive interaction represented by $\beta(-Q_{st})$. Similarly, D_{s0} is probably estimated by Eq. 11 by considering the change of various parameters, such as λ, v_f, m, C, ΔE_v, and V, due to the adsorptive interaction. The approximation of D_{s0}, however, is not sufficient because the parameters in Eqs. 10 and 11 cannot be accurately estimated in a potential field of adsorption. It was recommended in the absolute-rate theory that the parameters should be calculated on the basis of the intrinsic properties of both a solvent and an adsorbate by considering their molar fractions. However, the molar fractions of both the components in the neighborhood of the surface of an adsorbent cannot be exactly determined. Although a sufficiently strict estimation of D_{s0} cannot be attained, D_{s0} may be close to D_{m0} under the conditions that the molecular properties of the solvent and adsorbate are similar to each other. It has been confirmed that the values of D_{s0} and D_{m0} are almost of the same order of magnitude in many cases. In conclusion, the following equations were derived for D_s at zero surface coverage of an adsorbate (Miyabe and Takeuchi, 1997):

$$D_s = D_{s0}\exp\{-[E_m + \beta(-Q_{st})]/R_gT\} \tag{17}$$

$$D_s = D_{s0}\exp\{-[\alpha\Delta E_v + \beta(-Q_{st})]/R_gT\}. \tag{18}$$

The dependence of D_s on temperature and the amount adsorbed are characteristic features of surface diffusion. A number of studies on surface diffusion have been made from the standpoints of the temperature and concentration dependence of D_s. The temperature dependence of D_s has usually been represented by using the Arrhenius-type function similar to other activated processes. On the other hand, the concentration dependence of D_s has been interpreted by taking into account the change in $(d \ln c/d \ln q)$ or Q_{st} resulting from the variation in q. By considering the chemical-potential driving force, D_s at a certain amount adsorbed, $D_s(q)$, can be expressed on the basis of D_s at zero surface coverage, $D_s(0)$, as follows:

$$D_s(q) = D_s(0)\,(d\ln c/d\ln q). \tag{19}$$

By combining Eqs. 17 and 19,

$$D_s(q) = D_{s0}(d\ln c/d\ln q)\exp\{-[E_m + \beta(-Q_{st})]/R_gT\}. \tag{20}$$

The change in Q_{st} due to the change in q was considered in connection with the change in E_{ap} (Miyahara and Okazaki, 1992, 1993; Urano et al., 1981):

$$Q_{st} = q_{st} - E_{ap} \tag{21}$$

$$Q_{st} = q_{st} - R_gT\ln(c_s/c), \tag{22}$$

where q_{st} is an isosteric heat of adsorption at $c = c_s$, and may be constant irrespective of q. Urano et al. (1981) claimed that q_{st} was equal to the heat of solution, ΔH_{sol}. Substituting Eq. 20 into Eq. 21, the following equation is obtained:

$$D_s(q) = D_{s0}(d\ln c/d\ln q)\exp\{-[E_m + \beta(-q_{st} + E_{ap})]/R_gT\}. \tag{23}$$

In Eq. 23, the influence of q on D_{s0} is not taken into account. The value of $D_s(q)$ can be calculated by Eq. 23 on the assumption that D_{s0} does not seriously change with the variation in q. The concentration dependence of D_s is quantitatively interpreted in terms of the change in both $(d\ln c/d\ln q)$ and E_{ap} in Eq. 23. It is also expected that Eq. 23 provides a consistent explanation to the temperature dependence of D_s.

Moment Analysis

Chromatographic peaks were analyzed by the method of moments (Suzuki, 1973, 1990). The details of the method were described in previous articles (Miyabe and Suzuki, 1992, 1994a, 1995). Information about adsorption equilibrium and mass-transfer rates in a column was obtained from first- and second-moment analyses, respectively. In this study, some corrections were made in order to estimate D_s from second moments. The influence of the corrections on D_s value is considered. The uncertainty in the estimation of D_m fluid-to-particle mass-transfer coefficient, k_f, and pore diffusivity, D_p, influences the determination of D_s.

Accuracy of the estimation of D_m must be considered. The value of D_m was calculated by the Wilke–Chang equation (Reid et al., 1987). It was reported that D_m could be estimated by the equation with an average error of about 10%. Although several other correlations have also been proposed, the average error is less than 10% in many cases. The influence of three parameters—the concentration of the solute, viscosity of the solvent, η, and the temperature—on the estimation of D_m is considered. It was reported that the correlations were applied for concentrations of a solute up to about 5 or 10 mol % in engineering works. In this study, the maximum concentration of an adsorbate, *p-tert*-octylphenol (PTOP), was 0.12 mol %. The concentration of PTOP was relatively low. It was generally reported that D_m was frequently proportional to $\eta^{-0.5}$. In this study, the viscosity of PTOP solutions was increased from 1.55 mPa·s (70 vol. % methanol) to 1.57 mPa·s (0.12 mol % PTOP solution) at 298 K. The influence of the change in η of the solutions on the estimation of D_m was negligible because the change in η was quite small and the values of η were sufficiently low. For the Wilke–Chang equation, the following correlation was assumed for the interpretation of the influence of temperature on the estimation of D_m:

$$D_m\eta/T = \text{constant}. \tag{24}$$

Several other correlations were also proposed for the temperature dependence of D_m. An average error of about 10% was reported. In this study, measurements of chromatographic peaks were made in the temperature range from 288 K to 308 K. The change in temperature was not so large. In conclusion, the values of D_m seem to be estimated with an error less than about 10%.

An intraparticle diffusivity, D_e, was determined from second moments by subtracting the contribution of fluid-to-particle mass-transfer to peak spreading. The uncertainty in the estimation of k_f also influences the accuracy of D_s. The Wilson–Geankoplis (1966) equation was used for the estimation of k_f. The value of k_f is proportional to two-thirds of the power of D_m. If D_m is estimated with an error less than about 10% as described earlier, the discrepancy between the values of k_f calculated from the different D_m values seems to be less than about 6%. Different values of k_f may also be estimated by applying various correlations previously proposed in the literature, even if an identical value of D_m is used. For example, k_f for benzene at 298 K was calculated as 1.85×10^{-2} $\mathrm{cm \cdot s^{-1}}$ according to the Wilson–Geankoplis equation under the conditions that a superficial velocity of 70 vol. % methanol was 0.12 $\mathrm{cm \cdot s^{-1}}$ and D_m of benzene was 8.2×10^{-6} $\mathrm{cm^2 \cdot s^{-1}}$. Another value of k_f was obtained as 1.48×10^{-2} $\mathrm{cm \cdot s^{-1}}$ under the same conditions by the following equation proposed by Kataoka et al. (1972):

$$Sh = 1.85 [(1 - \epsilon)/\epsilon]^{1/3} Sc^{1/3} Re_p^{1/3}. \tag{25}$$

The resulting value of D_s calculated by taking k_f as 1.48×10^{-2} $\mathrm{cm \cdot s^{-1}}$ was 3.3×10^{-6} $\mathrm{cm^2 \cdot s^{-1}}$. Compared with the original value of D_s, 2.7×10^{-6} $\mathrm{cm^2 \cdot s^{-1}}$, both values were of the same order of magnitude. As indicated in previous articles (Miyabe and Suzuki, 1994a,b, 1995), the contributions of three mass-transfer processes in a column—axial dispersion, fluid-to-particle mass transfer, and intraparticle diffusion—were almost of the same order of magnitude in many cases of RP-LC systems. It is concluded that errors in the estimation of k_f may not seriously influence the determination of D_s.

The contribution of D_p to D_e was corrected when D_s was calculated from D_e. The accuracy in the estimation of D_p also influences the accuracy of D_s. In this study, D_p was calculated from D_m according to the parallel-pore model. In such a case, the uncertainty of the estimation of D_p corresponds to that of D_m. From the consideration about the uncertainty of the estimation of D_m, the error for D_p is probably about 10% or less. As indicated in previous articles (Miyabe and Suzuki, 1992, 1993b, 1994a,b, 1995), the contribution of surface diffusion to overall mass transfer in RP packing materials is usually as much as about 85–95% or above. Because surface diffusion has an extremely dominant role for intraparticle diffusion, the influence of the variation in the estimation of D_p on the determination of D_s is negligible. On the basis of the considerations described earlier, it is concluded that D_s was probably calculated with an error of several percent.

Experiments

Experimental conditions in this study are listed in Table 1. Pulse-response experiments were made at various surface coverages of PTOP by varying both column temperature and the flow rate of a mobile phase. Chromatographic peaks were analyzed by the moment method. Information on experimental techniques in other studies is also summarized in Table 2. The details of each work can refer to original articles (Itaya et al., 1984, 1987; Miyabe and Suzuki, 1992; Suzuki and Fujii, 1982).

Table 1. Properties of ODS Columns and Experimental Conditions

Column	ODS	ODS
Average particle diameter [μm]	24	45
Porosity	0.43	0.47
Particle density [$\mathrm{g \cdot cm^{-3}}$]	0.87	0.86
Carbon content [wt. %]	17.7	17.1
Functionality	Monomeric	Monomeric
Column size [mm]	6 ID × 150	
Void fraction	0.38	0.43
Tortuosity factor	4.9	4.6
Mass of adsorbent [g]	2.3	2.2
Column temperature [K]	298	288–308
Mobile phase	Methanol/water 70/30 (vol.)	
Superficial velocity [$\mathrm{cm \cdot s^{-1}}$]	0.06–0.12	
Sample materials	*p-tert*-Octylphenol (PTOP)	
Inert substance	Uracil	

Results and Discussion

Adsorption equilibrium

Adsorption isotherms of PTOP on ODS–silica gel at various temperatures were measured by the breakthrough experiments. The correlations between $1/q$ and $1/c$ are illustrated in Figure 1. Straight correlations having different slopes were obtained. The slope of the correlations showed temperature dependence. In contrast, the linear lines passed through the same intercept irrespective of temperature, indicating that the adsorption isotherms of PTOP on ODS–silica gel could be represented by the Langmuir equation,

$$q = q_0 K_L c/(1 + K_L c). \tag{26}$$

In an earlier article (Miyabe and Suzuki, 1991), the authors reported that the adsorption equilibrium of RP-LC could be expressed by the Toth equation when the parameter t was close to unity:

$$q = abc/(b^t + c^t)^{1/t}. \tag{27}$$

The Toth equation is identical to the Langmuir isotherm at $t = 1$. A similar result was obtained when the particle diameter of ODS–silica gel was 24 μm. Isosters for various amounts adsorbed were calculated by the Langmuir parameters, that is, q_0 and K_L, which were obtained from the correlations in Figure 1. Analysis of temperature dependence of the isosters provided Q_{st} at each surface coverage of PTOP. The value of $(-Q_{st})$ was about 16 to 18 $\mathrm{kJ \cdot mol^{-1}}$ regardless of the amount adsorbed and the particle size of ODS–silica gel. The constant values of Q_{st} suggest an energetic homogeneity of the ODS surface. The value of E_{ap} is probably constant during the progress of adsorption in the RP-LC system.

Influence of amount adsorbed on surface-diffusion coefficient

Pulse-response experiments were carried out at various surface coverages of PTOP, which was increased up to about

Table 2. Comparison of Experimental Techniques and Results

Reference	Miyabe and Suzuki, 1992	Suzuki and Fujii, 1982	Itaya et al., 1984, 1987
Experimental conditions			
Isotherm	Langmuir $q = q_0 K_L c/(1 + K_L c)$	Freundlich $q = K_F c^{1/n}$	Jossens $c = (q/H)\exp(K_j q^p)$
Adsorbent	ODS-silica gel	Activated carbon (HGR513)	Amberlite XAD-4, XAD-7
Solvent	Methanol/water (70/30, v/v)	Water	Water
Adsorbate	*p-tert*-Octylphenol (PTOP)	Propionic acid	Phenol
Temperature	288, 298, 308 K	293, 303, 313 K	303 K
Method	Pulse response—moment analysis	Steady-state diffusion experiment	Batch adsorption
Concentration dependence			
$d \ln c/d \ln q$	$1 + K_L c$ Not constant	n Constant	$1 + K_j p q^p$ Not constant
Q_{st}	Constant	Not constant	Not constant
E_{ap}	Constant	Not constant	Not constant
Results			
β(average)	0.31	0.56	0.25 (XAD-4), 0.55 (XAD-7)
q_{st}	Not determined	-5.9 kJmol^{-1}	-9.2 kJmol^{-1} (XAD-4), -1.9 kJmol^{-1} (XAD-7)
Remarks	Concentration dependence of D_s is attributed to the change in $(d \ln c/d \ln q)$, and cannot be explained by considering the change in Q_{st} and E_{ap}.	Concentration dependence of D_s is attributed to the change in Q_{st}/E_{ap}, and cannot be explained by considering the change in $(d \ln c/d \ln q)$.	Concentration dependence of D_s is attributed to the change in both Q_{st} (E_{ap}) and $(d \ln c/d \ln q)$, and can be interpreted by Eq. 23.
	Both temperature and concentration dependence of D_s can be interpreted by Eq. 20 or Eq. 23.	Both temperature and concentration dependence of D_s can be interpreted by Eq. 23.	No information was obtained for the applicability of Eq. 23 to the interpretation of temperature dependence of D_s.

60% of the saturated amount adsorbed, or about 0.67 mmol·g^{-1}. The value of D_s increased by a factor of about 2 to 3 with an increase in the amount of PTOP adsorbed. Figure 2 postulates D_s at each amount adsorbed. When the particle diameter of ODS-silica gel was 24 μm, a similar change in D_s was observed at 298 K.

According to the Arrhenius equation, E_s at various surface coverages was determined from the temperature dependence of D_s at each amount adsorbed. Resulting values of E_s were about 25 to 28 kJ·mol^{-1} (45 μm, $q = 0 \sim 0.3$ mmol·g^{-1}) and about 30 kJ·mol^{-1} (24 μm, $q = 0$ mmol·g^{-1}), irrespective of

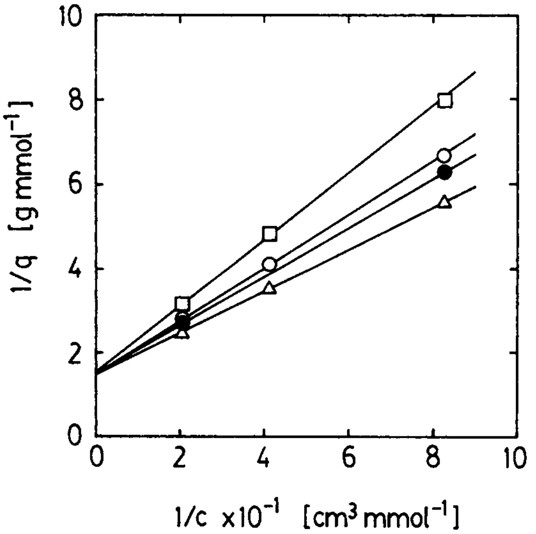

Figure 1. Langmuir plot of adsorption equilibrium data of PTOP on ODS-silica gel.

Keys: refer to Figure 2.

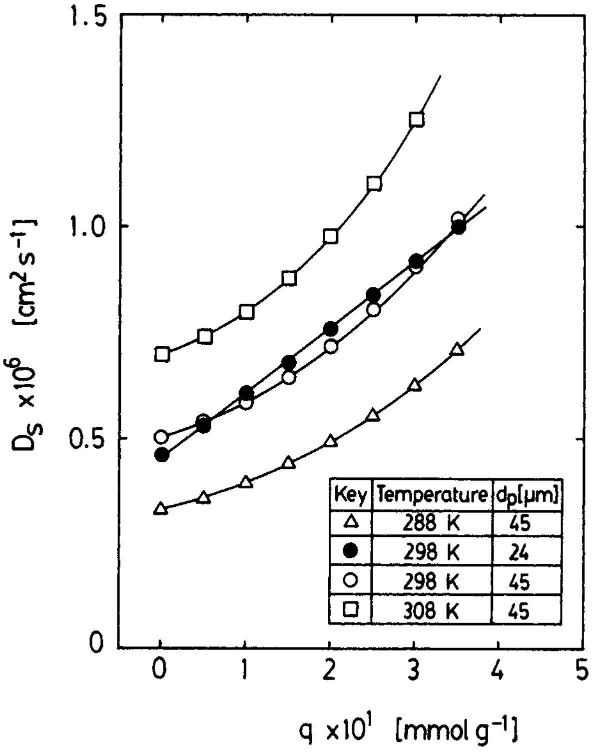

Figure 2. Concentration dependence of D_s.

q. The almost constant E_s is consistent with the results that Q_{st} is also constant regardless of q, and that adsorption isotherms can be expressed by the Langmuir equation. These results indicate that the surface of ODS–silica gel is regarded as an energetically homogeneous surface.

As mentioned earlier, E_s was larger than $(-Q_{st})$ in the RP-LC system in this study. Similar relationships were observed in other liquid-phase adsorption systems (Awum et al., 1988; Ching et al., 1989; Ma et al., 1988; Miyabe and Suzuki, 1993b, 1994a, 1995). The presence of surface-diffusion phenomena can be denied under such conditions. On the contrary, smaller values of E_s compared with $(-Q_{st})$ have also been reported (Muraki et al., 1982; Suzuki and Fujii, 1982). The authors interpreted the various situations of the correlation between E_s and Q_{st} by applying the restricted molecular diffusion model for surface diffusion. A formulation of D_s in the model was derived on the basis of the absolute-rate theory (Miyabe and Takeuchi, 1997).

Interpretation for temperature and concentration dependence of surface-diffusion coefficient

Equation 23 was applied to quantitative analyses of characteristic features of surface-diffusion phenomena in the various liquid-phase adsorption systems, that is, the Langmuir, Freundlich, and Jossens-type systems. The results are compared with each other in Table 2.

Langmuir-type Adsorption. Equation 23 includes two factors, which vary with the change in q. One is $(d \ln c/d \ln q)$, which is a logarithmic slope of an adsorption isotherm. The other is E_{ap}, which changes according to the energetic heterogeneity of the surface of an adsorbent. As described earlier, no significant change in Q_{st} and E_s due to the change in q was observed in the RP-LC system in this study. Adsorption isotherms can also be represented by the Langmuir equation. These results indicate that the concentration dependence of D_s in Figure 2 cannot be explained by considering the change in Q_{st} and E_{ap}.

As illustrated in Figure 3, linear correlations having a slope of about unity were confirmed between ln $D_s(q)$ and ln $(d \ln c/d \ln q)$ at each temperature. In spite of the difference in the particle diameter, a similar correlation was observed for ODS–silica gel of 24 μm at 298 K. The results in Figure 3 indicate that the positive concentration dependence of D_s is attributed to the change in $(d \ln c/d \ln q)$, as described in Eq. 19. Figure 4 illustrates the correlations between $(\ln D_s + E_s/R_gT)$ and $(d \ln c/d \ln q)$ according to Eqs. 16 and 20. It was assumed that D_{s0} was independent of q. The data at different temperatures could be correlated with a single straight line having a slope of unity. It is concluded from the results in Figure 4 that Eq. 20 can provide a consistent interpretation for both the temperature and concentration dependence of D_s in the Langmuir-type adsorption, for example, in RP-LC systems using ODS–silica gel as a stationary phase.

Freundlich-type Adsorption. The effectiveness of Eq. 20 was proved for the quantitative interpretation of the temperature and concentration dependence of D_s in the case that adsorption equilibrium can be expressed by the Langmuir isotherm. In order to confirm the validity of Eq. 20, experimental results of surface diffusion in two liquid-phase adsorption systems other than the Langmuir type were analyzed by applying Eq. 20. Although a number of studies on surface diffusion in liquid-phase adsorption have been reported, a few studies have been carried out in which thermodynamic properties are also quantitatively determined as well as adsorption equilibrium and surface-diffusion coefficients. As an example of the Freundlich-type adsorption, the equilibrium, kinetic, and thermodynamic data reported by Suzuki and Fujii (1982) were analyzed by applying Eq. 20. They studied an aqueous adsorption of propionic acid onto an activated carbon by means of steady-state diffusion experiments. The Fre-

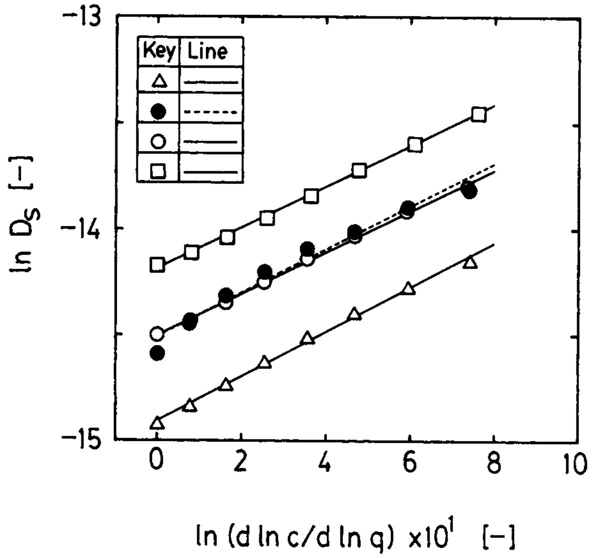

Figure 3. Correlation between ln D_s and ln $(d \ln c/d \ln q)$.

Keys: refer to Figure 2.

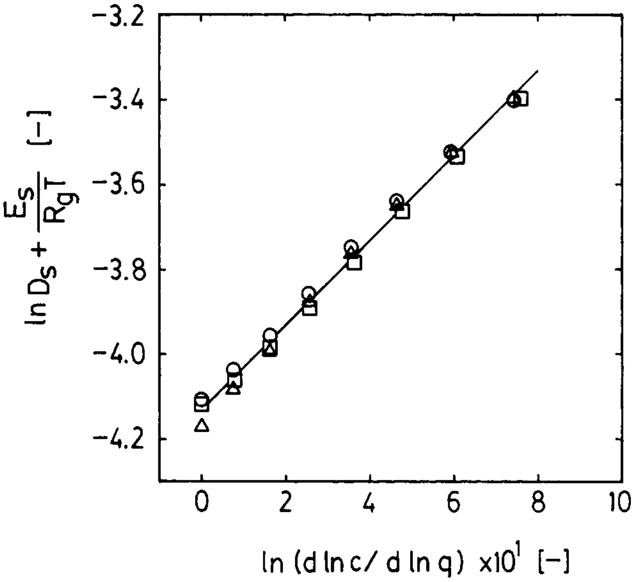

Figure 4. Correlation between $(\ln D_s + E_s/R_gT)$ and ln $(d \ln c/d \ln q)$ in a Langmuir-type adsorption system.

Keys: refer to Figure 2.

undlich equation represents adsorption equilibrium in the aqueous adsorption of propionic acid:

$$q = K_F c^{1/n}. \tag{28}$$

A remarkable concentration dependence of D_s was interpreted in terms of the change in the heat of adsorption resulting from the change in q. When an adsorption isotherm can be represented by the Freundlich equation, the value of $(d \ln c/d \ln q)$ is identical to n, which is assumed to be constant irrespective of q. It is predicted that the consideration from the standpoint of the term of $(d \ln c/d \ln q)$ provides no contribution to the interpretation for the concentration dependence of D_s. Contrary to the case of Langmuir-type adsorption, the change in D_s must be considered in connection with the change in Q_{st} or E_{ap}. On the other hand, it was reported that the value of n slightly varied with temperature (Suzuki and Fujii, 1982).

Figure 5 shows several correlations analyzed by Eq. 20. The value of $[\ln D_s + E_m/R_gT - \ln(d \ln c/d \ln q)]$ is plotted as ordinate, and that of $(-Q_{st}/R_gT)$ as abscissa. The frequency factor D_{s0} was assumed to be constant irrespective of q. The experimental plots were scattered around slightly curved lines, which were close to each other irrespective of temperature. Although sufficient linearity was not obtained, a single correlation seemed to express the trends of the experimental data at different temperatures. An average slope calculated from the plots in Figure 5 was about 0.56, indicating that propionic acid molecules adsorbed on the surface of the activated carbon must gain an activation energy equal to 56% of $(-Q_{st})$ in order to jump into the next hole. The slightly curved profile is probably caused by the change in D_{s0}. If the several parameters, such as λ, v_f, C, ΔE_v, included in Eqs. 10 and 11 vary significantly with q, D_{s0} must also indicate a concentration dependence. Equation 20 cannot completely take into account the concentration dependence of D_{s0}. However, it may be possible that D_{s0} is regarded to be almost constant because of the degree of the curvature of the plots in Figure 5. The results in Figure 5 demonstrate that Eq. 20 is effective for the consistent analysis of the temperature and concentration dependence of D_s in the Freundlich-type adsorption system. Suzuki and Fujii (1982) suggested that the change in Q_{st} with q was probably not the only explanation for the remarkable concentration dependence of D_s, and claimed the necessity of further accumulation of accurate experimental data of D_s in various adsorption systems in order to elucidate the surface-diffusion mechanism.

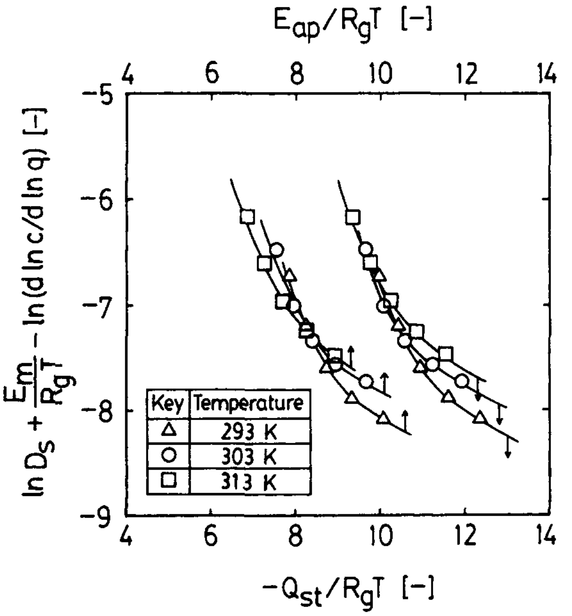

Figure 5. Correlation between $[\ln D_s + E_m/R_gT - \ln(d \ln c/d \ln q)]$ and $(-Q_{st}/R_gT)$ or (E_{ap}/R_gT) in a Freundlich-type adsorption system.

The parameters β and q_{st} in Eq. 23 are assumed to be independent of q. Figure 5 also illustrates the correlations between $[\ln D_s + E_m/R_gT - \ln(d \ln c/d \ln q)]$ and (E_{ap}/R_gT). The parallel correlations in Figure 5 indicated that the change in Q_{st} resulted from the change in E_{ap} due to the change in q. The value of $(-q_{st})$ calculated from the change in both Q_{st} and E_{ap} with q was about 5.9 kJmol^{-1}. These results suggest the validity of Eq. 23.

Jossens-type Adsorption. Itaya et al. (1984, 1987) studied aqueous adsorption of phenol derivatives onto macroreticular polymeric adsorbents Amberlite XAD-4 and XAD-7. It was concluded that the adsorption equilibrium could be most adequately represented by applying the equation derived by Jossens et al. (1978),

$$c = (q/H)\exp(K_J q^p). \tag{29}$$

The dependence of D_s on q was quantitatively analyzed at various temperatures. Thermodynamic properties of liquid-phase adsorption, such as Q_{st} and E_s, were also determined. A quantitative analysis of the experimental data reported by Itaya et al. (1984, 1987) was carried out as an example of a liquid-phase adsorption other than the Langmuir and Freundlich type. In this case, $(d \ln c/d \ln q)$ can be calculated as follows:

$$d \ln c/d \ln q = 1 + K_J p q^p. \tag{30}$$

Itaya et al. measured equilibrium and kinetic data for several adsorbates at various temperature conditions. However, a coincident temperature, at which both equilibrium and kinetic data were determined, was only 303 K. The experimental data for phenol at 303 K were also analyzed by Eq. 20. Resultant plots are illustrated in Figure 6. The ordinate and abscissa of Figure 6 are the same as those in Figure 5. In the same manner, the value of D_{s0} was assumed to be constant irrespective of q. Sufficiently linear correlations were observed between $[\ln D_s + E_m/R_gT - \ln(d \ln c/d \ln q)]$ and $(-Q_{st}/R_gT)$ for XAD-7. A slightly curved profile was observed for XAD-4. Average slopes calculated from the plots in Figure 6 were about 0.25 and 0.55 for XAD-4 and XAD-7, respectively. It was indicated that phenol molecules adsorbed on the surface of the adsorbents must gain an activation energy equal to 25% or 55% of $(-Q_{st})$ in order to jump into the next hole. Although the concentration dependence of D_{s0} was not taken into account, the results in Figure 6 may indicate almost constant values of D_{s0} because of the linearity and the slight curvature of the correlations in Figure 6.

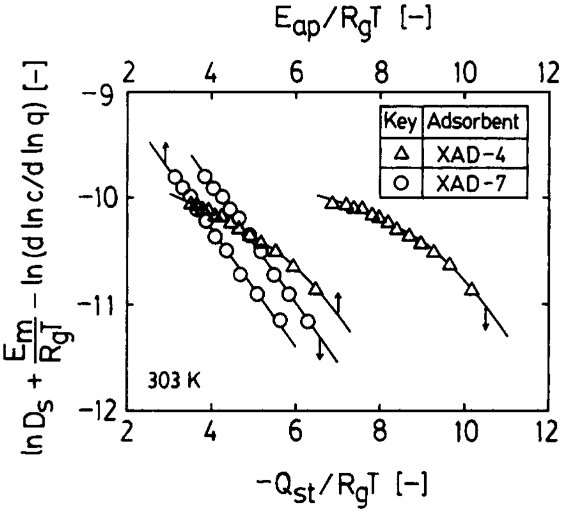

Figure 6. Correlation between $[\ln D_s + E_m/R_gT - \ln(d\ln c/d\ln q)]$ and $(-Q_{st}/R_gT)$ or (E_{ap}/R_gT) in a Jossens-type adsorption system.

Similar to the results in Figure 5, parallel correlations were confirmed between $[\ln D_s + E_m/R_gT - \ln(d\ln c/d\ln q)]$ and (E_{ap}/R_gT) in Figure 6. It was again concluded that the change in Q_{st} resulted from the change in E_{ap} due to the change in q for the Jossens-type adsorption as well as the Freundlich type. The value of $(-q_{st})$ calculated from the change in Q_{st} with q was about 9.2 kJ·mol^{-1} and 1.9 kJ·mol^{-1} for XAD-4 and XAD-7, respectively. The valve of ΔH_{sol} of phenol into water was calculated at about 7.2–9.5 kJ·mol^{-1} from the temperature dependence of the solubility of phenol into water. The value of $(-q_{st})$ for XAD-4 was comparable to the value of ΔH_{sol}. However, an explanation has not yet been provided for the smaller value for XAD-7. A strict study on physicochemical correlations between solvent molecules and adsorbents must be required for the quantitative analysis of q_{st}. The results in Figure 6 also seemed to prove the usefulness of Eq. 23. In order to prove the validity of Eq. 23 in more detail, exact measurements and quantitative analyses of D_s must be made in various adsorption systems, which is a subject currently studied.

Conclusion

A restricted molecular diffusion model was proposed for the analysis of surface-diffusion phenomena. As a formula of D_s, Eq. 23 was derived on the basis of the absolute-rate theory. Equation 23 was applied to quantitative analyses of characteristic features of surface-diffusion phenomena in the various liquid-phase adsorption systems consisting of solvents and adsorbates with similar molecular properties. It was demonstrated that Eq. 23 was effective for a consistent explanation of the dependence of D_s on both temperature and the amount adsorbed in the Langmuir-, Freundlich-, and Jossens-type systems.

In Langmuir-type adsorption, the concentration dependence of D_s could be interpreted in terms of the change in $(d\ln c/d\ln q)$. No change in E_{ap} was expected. On the contrary, $(d\ln c/d\ln q)$ does not vary in Freundlich-type adsorption. An analysis from the standpoint of the change in $(d\ln c/d\ln q)$ could not provide an efficient interpretation for the concentration dependence of D_s. The change in Q_{st} was attributed to the change in E_{ap}. Both the temperature and concentration dependence of D_s in Freundlich-type adsorption were consistently interpreted by applying Eq. 23. In the case of the Jossens-type adsorption, the variation of D_s due to the change in q could be interpreted by taking into account the change in both $(d\ln c/d\ln q)$ and E_{ap}. In conclusion, in the various liquid-phase adsorption systems, the validity of Eq. 23 was proved by means of quantitative analyses of the previously published experimental results. In order to elucidate the surface-diffusion mechanism of liquid-phase adsorption, further accumulation and quantitative analysis of accurate experimental data of D_s are required in various adsorption systems.

Notation

a = parameter in the Toth equation (Eq. 27), cm^3·g^{-1}
b = parameter in the Toth equation (Eq. 27), mmol·cm^{-3}
c = concentration of an adsorbate in a bulk phase, mmol·cm^{-3}
C = constant in Eq. 10
c_s = saturated concentration of an adsorbate in a bulk phase, mmol·cm^{-3}
D_{m0} = frequency factor of molecular diffusion, cm^2·s^{-1}
E_z = axial dispersion coefficient, cm^2·s^{-1}
H = Henry constant, cm^3·g^{-1}
h = Planck's constant, J·s
K = adsorption equilibrium constant, cm^3·g^{-1}
k = Boltzmann's constant, J·K^{-1}
K_F = Freundlich's constant, cm^3·g^{-1}
K_J = parameter in the Jossens equation (Eq. 29), (mol^{-1})^p
m = molecular weight, mol^{-1}
n = Freundlich constant
N_A = Avogadro number, mol^{-1}
p = parameter in the Jossens equation (Eq. 29)
q_0 = adsorption capacity, mmol·g^{-1}
R_g = gas constant, J·mol^{-1}·K^{-1}
T = temperature, K
V = molar volume, cm^3·mol^{-1}
v_f = free volume, cm^3
α = ratio of E_m to ΔE_v
α' = ratio of E_s to $(-Q_{st})$
β = ratio of E_b to $(-Q_{st})$

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