

# Analysis of Surface Diffusion Phenomena in Liquid Phase Adsorption

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Received: March 10, 1997; In Final Form: June 11, 1997<sup>©</sup>

A model for surface diffusion was proposed on the basis of molecular diffusion. Surface diffusion was regarded as a molecular diffusion restricted due to the adsorptive interaction between adsorbate molecules and the surface of adsorbents. The restricted molecular diffusion model was formulated by applying the absolute rate theory. Experimental data of surface diffusion coefficient in reversed-phase liquid chromatography were analyzed by considering the influence of the adsorptive interaction. Though accurate specification of a frequency factor was not sufficient, characteristic features of the activation energy of surface diffusion could be quantitatively interpreted. The activation energy of surface diffusion was divided into two contributions of a hole-making step and a jumping one. The former was correlated with the evaporative energy of a solvent, not of an adsorbate, and the latter with the isosteric heat of adsorption of the adsorbate. The validity of the concept was proved by applying the model to the quantitative analysis of surface diffusion data on other various liquid phase adsorption previously published. An interpretation was provided for various correlations between the activation energy of surface diffusion and isosteric heat of adsorption in the liquid phase adsorption systems.

## Introduction

It is well-known that surface diffusion has a significant contribution to intraparticle diffusion in porous adsorbents in various adsorption systems.<sup>1,2</sup> The dependence of a surface diffusion coefficient,  $D_s$ , on the amount adsorbed and temperature has been analyzed as characteristic features of surface diffusion. On the basis of the results, the mechanism of surface diffusion has been discussed by applying various models. The temperature dependence of  $D_s$  has been usually analyzed by the Arrhenius equation by considering surface diffusion as an activated process.

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

where  $D_{s0}$  and  $E_s$  are the frequency factor and activation energy of surface diffusion, respectively,  $R_g$  is the gas constant, and  $T$  is temperature. On the other hand, Gilliland *et al.*<sup>3,4</sup> interpreted the concentration dependence of  $D_s$  in gas phase adsorption by considering the change in the heat of adsorption resulted from the change in the amount adsorbed. The value of  $E_s$  was approximated as a certain fraction of the heat of adsorption as follows.

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

where  $Q_{st}$  is an isosteric heat of adsorption. The coefficient  $\alpha'$  is positive and is usually smaller than unity for surface diffusion in gaseous systems. By substituting eq 2 into eq 1

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

Surface diffusion phenomena in liquid phase adsorption have also been studied from mainly the concentration and temperature dependence of  $D_s$  on the basis of the ordinary equation, eq 3.<sup>1,2</sup> The concentration dependence of  $D_s$  has been interpreted by considering the change in the heat of adsorption or in the logarithmic slope of an adsorption isotherm, ( $d \ln c/d \ln q$ ), due to the variation in the amount adsorbed. Various correla-

tions have been proposed, in which  $D_s$  is represented as a function of the amount of adsorbed.<sup>5–8</sup>

The mechanism of surface diffusion in liquid phase adsorption has also been analyzed on the basis of the absolute rate theory. Komiya and Smith<sup>9,10</sup> studied the correlation between  $D_s$  and the bond energy of adsorbate molecules with the surface of adsorbents. It was reported that an increase in methanol content in solvents was accompanied with both a decrease in adsorption capacity and an increase in  $D_s$ . They tried to explain the results in terms of a two-step theory based on the Eyring's rate theory. The activation process of surface migration was considered to be consist of two conceptual steps, *i.e.*, a hole-making step and a jumping one. The contribution of the jumping step to  $E_s$  was correlated with the heat of adsorption. Itaya *et al.*<sup>11</sup> determined  $D_s$  in an aqueous adsorption of phenol derivatives onto macroporous resins by finite bath adsorption experiments. The linear correlation between  $E_s$  and  $Q_{st}$  was indicated by analyzing the concentration dependence of  $D_s$ . By applying the concept of molecular diffusion to surface diffusion, they suggested that the slope and intercept of the linear relation corresponded to the contributions of a jumping step and hole-making one, respectively. This conclusion is in accord with that of Komiya and Smith.<sup>9,10</sup> Miyahara and Okazaki<sup>12,13</sup> showed a significant concentration dependence of  $D_s$  of benzene derivatives in aqueous adsorption onto an activated carbon by batch kinetic experiments. They attempted to explain the concentration dependence of  $D_s$  by applying Eyring's rate theory. They assumed that the rate-controlling step was a hole-making step under a potential field of adsorption. The activation energy of surface diffusion was assumed to be a certain fraction of the sum of both the evaporative energy of an adsorbate and the adsorption potential. Interpretation of the influence of both the concentration and temperature on  $D_s$  was demonstrated for the aqueous adsorption. These studies dealt with the physical meaning of thermodynamic properties in surface diffusion processes on the basis of the absolute rate theory.

If there are no adsorbate molecules adsorbed onto the surface of an adsorbent, no surface diffusion occurs. Alternatively, the presence of surface diffusion phenomena is expected if only the adsorptive interaction between adsorbate molecules and the surface of an adsorbent is present, even though the intensity of

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<sup>©</sup> Abstract published in *Advance ACS Abstracts*, September 1, 1997.

TABLE 1: Properties of Columns and Experimental Conditions

column	TMS	C4	C8	ODS	ODS
av particle diam, $d_p$ ( $\mu\text{m}$ )	45	45	45	45	45
particle density, <sup>a</sup> $\rho_p$ ( $\text{g cm}^{-3}$ )	0.74	0.73	0.75	0.86	0.81
porosity, <sup>a</sup> $\epsilon_p$	0.62	0.61	0.55	0.46	0.37
pore volume ( $\text{cm}^3 \text{g}^{-1}$ )	0.87	0.84	0.85	0.68	0.68
specific surface area ( $\text{m}^2 \text{g}^{-1}$ )	216	211	212	184	184
carbon content (wt %)	4.1	6.7	9.9	17.1	17.1
mass of adsorbent (g)	1.9	1.8	1.8	2.1	2.1
ligand amount ( $\text{mmol g}^{-1}$ )	1.2	0.93	0.83	0.71	0.71
ligand density ( $\text{nm}^{-2}$ )	2.7	2.2	2.0	1.9	1.9
column size (mm)			6 i.d. $\times$ 150		
void fraction, <sup>a</sup> $\epsilon$	0.44	0.42	0.42	0.43	0.39
tortuosity factor, <sup>a</sup> $k^2$	4.1	4.6	4.4	4.5	5.5
column temperature (K)			288–308		
mobile phase	methanol/water: 70/30 (vol)	methanol/water: 70/30 (vol)	methanol–water: 70/30 (vol)	methanol/water: 70/30 (vol)	acetonitrile/water: 70/30 (vol)
superficial velocity, $u_0$ ( $\text{cm s}^{-1}$ )			0.06–0.12		
sample materials		benzene derivatives, polyaromatic hydrocarbons			

<sup>a</sup> The values were determined by means of the pulse response experiments with sodium nitrate and uracil.

the interaction is quite weak. However, critical conditions concerning the presence and absence of surface diffusion phenomena have not yet been elucidated. With respect to this subject, eq 3 cannot provide an adequate conclusion. Equation 3 obviously indicates that  $D_s$  is close to  $D_{s0}$  when  $Q_{st}$  is nearly equal to zero. In various liquid phase adsorption systems,<sup>7,9,10,14–16</sup> experimental values of  $D_{s0}$  have been reported to be ranging from about  $10^{-4}$  to  $10^{-1} \text{ cm}^2 \text{ s}^{-1}$ . On the contrary, molecular diffusivity,  $D_m$ , is usually estimated as the values of the order of about  $10^{-5} \text{ cm}^2 \text{ s}^{-1}$  by applying various correlations such as the Wilke–Chang equation.<sup>17</sup> It is indicated that  $D_s$  is several orders of magnitude larger than  $D_m$  under the conditions that the adsorptive interaction is negligible. This conclusion obtained from eq 3 may be unreasonable, suggesting that applicable conditions of eq 3 are not specified. It cannot be concluded that eq 3 is available to kinetic studies on surface diffusion phenomena from the viewpoint of the intensity of the adsorptive interaction. Development of a different formula relating to  $D_s$  must be required in order to specify the mechanism of surface diffusion in more detail.

Surface diffusion is mass-transfer phenomena of adsorbate molecules under the adsorbed state. They probably migrate in a potential field of adsorption due to an adsorbent. The gain of  $E_s$  is required for the adsorbate molecules to surpass the boundary energy barrier between two adsorption sites. However, it is unnecessary that  $E_s$  is beyond the absolute value of  $Q_{st}$  because they do not need to be completely desorbed to a bulk phase. The ratio of  $E_s/(-Q_{st})$  should be positive and smaller than unity. In fact, the ratio is usually smaller than unity for surface diffusion in many gaseous adsorption systems.<sup>1,2</sup> On the contrary, larger values of  $E_s$  compared with  $(-Q_{st})$  have been frequently reported in liquid phase adsorption.<sup>14–16,18–23</sup> Under such conditions, it is energetically advantageous for adsorbate molecules to be desorbed from the surface of an adsorbent to a bulk phase rather than to migrate on the surface, suggesting that surface diffusion is absent. In other cases of liquid phase adsorption, however, the ratio of  $E_s/(-Q_{st})$  smaller than unity was also reported.<sup>7,24</sup> These contrary situations of thermodynamic properties in liquid phase adsorption cannot be consistently interpreted by eq 3 either.

In this paper, surface diffusion data in reversed-phase liquid chromatography were analyzed on the basis of molecular diffusion. A restricted molecular diffusion was proposed as one of models for the mechanism of surface diffusion. A formula for  $D_s$  was derived by considering the influence of the adsorptive interaction between adsorbate molecules and adsorbents on surface diffusion. The validity of the model was confirmed by

means of the analysis of experimental data in various liquid phase adsorption systems previously published. It was also demonstrated that various correlations between  $E_s$  and  $Q_{st}$  in liquid phase adsorption could be interpreted by applying the correlation proposed in this study.

### Experimental Section

**Apparatus.** Pulse response experiments were carried out by means of a high-performance liquid chromatograph equipment (LC-6A, Shimadzu). A small volume of sample solutions was injected into a fluid flow by use of a sample injector. Column temperature was kept at a constant level by using a thermostated water bath. A ultraviolet detector was employed to monitor the concentration of sample materials in effluent.

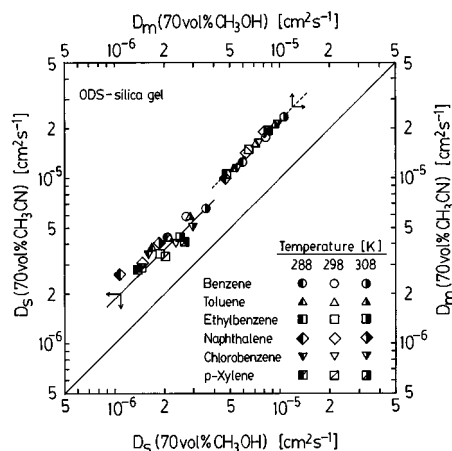
**Columns and Reagents.** Properties of commercial columns (YMC) are shown in Table 1. Four kinds of packing materials having various alkyl ligands were used, which seemed to be monofunctional.<sup>25</sup> The carbon number of the alkyl chains chemically bonded on the surface of silica gel was changed stepwise from 1 to 18 (TMS, C4, C8, and ODS). End capping of the packing materials, except of ODS, was not carried out. The density of the ligands was estimated by considering the carbon content of the packing materials and specific surface area of a base silica gel, *i.e.*,  $286 \text{ m}^2 \text{ g}^{-1}$ . It appeared that about 40–60% of silanol groups reacted with the alkyl ligands. The characteristic values of the surface of the packing materials were determined by nitrogen adsorption. Mobile phases were mixtures of an organic modifier, *i.e.*, methanol or acetonitrile, and water (70/30, vol).

**Procedure.** Experimental conditions are also listed in Table 1. Pulse response experiments were made at zero surface coverage of the adsorbates with varying both column temperature and the flow rate of the mobile phases. Measurements of chromatographic peaks were made by introducing small concentration perturbation pulses into the fluid flow. Chromatographic peaks measured were analyzed by the method of moments.<sup>2,26</sup> Details of the moment analysis of chromatographic peaks were described in previous papers.<sup>14,16,22,27</sup>

**Surface Diffusion Data in Literatures.** In this study,  $D_s$  at zero surface coverage of adsorbates was analyzed. If there were no experimental data, corresponding values of  $D_s$  were estimated by extrapolation of a concentration dependence curve of  $D_s$ . An error in the estimation of  $D_s$  may not provide so serious influence on the conclusion of this paper.

### Results and Discussion

**Correlation between Surface Diffusion and Molecular Diffusion.** Figure 1 illustrates the correlation between  $D_s$  of

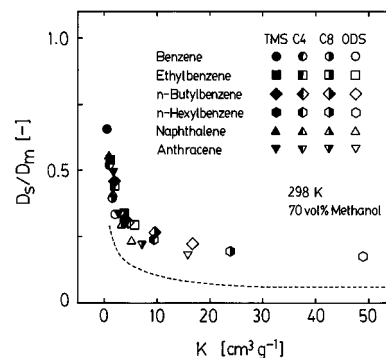


**Figure 1.** Comparison between surface diffusion coefficients and molecular diffusivities for methanol/water and acetonitrile/water mobile phase systems.

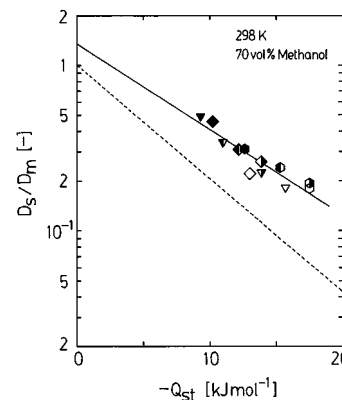
various adsorbates in two reversed-phase liquid chromatographic systems using methanol/water (70/30, vol) and acetonitrile/water (70/30, vol) as mobile phases. The values of  $D_s$  in 70 vol % acetonitrile were about 2 times larger than those in 70 vol % methanol. The ratio of the  $D_s$  values was almost constant regardless of temperature and the type of the adsorbates. The results in Figure 1 indicate that surface diffusion is evidently influenced by mobile phase conditions. Through the studies on adsorption equilibrium, Tanaka *et al.*<sup>28</sup> also suggested a penetration of mobile phase solvents into a stationary phase and an important role of the solvents on adsorption properties in reversed-phase liquid chromatography.

Figure 1 also shows the correlation of  $D_m$  estimated for the adsorbates in both mobile phase solvents. An almost straight relationship having a slope of unity was observed. The values of  $D_m$  of the adsorbates in 70 vol % acetonitrile were larger than those in 70 vol % methanol by a factor of about 2. The ratio of  $D_m$  in both solvents was sufficiently close to that of  $D_s$ . It is concluded that the difference in  $D_s$  may have resulted from that in  $D_m$ . The results in Figure 1 suggest the presence of a kind of correlation between  $D_s$  and  $D_m$ .

The influence of alkyl chain length of packing materials on adsorption characteristics in reversed-phase liquid chromatography was studied in connection with the adsorptive interaction between adsorbate molecules and adsorbents. The change in the alkyl chain length provides the change in hydrophobic adsorbability of the packing materials. The mechanism of surface diffusion, however, may be similar to each other. The correlation between  $D_s$  and the adsorptive interaction was studied by changing the hydrophobic adsorbability of the packing materials, which was caused by the change in the alkyl chain length. The influence of the adsorptive interaction on  $D_s$  is postulated in Figure 2. A decrease in adsorption equilibrium constant,  $K$ , is accompanied with an increase in  $D_s$ . The ratios of  $D_s/D_m$  scatter around a curved line, which may approach unity at  $K = 0$ . A similar tendency was observed for all the adsorbates. It is indicated that  $D_s$  is probably equal to  $D_m$  under the limiting conditions that the adsorptive interaction is negligibly small. The intensity of the adsorptive interaction is usually represented in terms of the heat of adsorption. Figure 3 illustrates the ratio of  $D_s$  to  $D_m$  as a function of  $-Q_{st}$ . An almost linear correlation was observed between  $\ln(D_s/D_m)$  and  $-Q_{st}$ . With a decrease in  $-Q_{st}$ ,  $D_s/D_m$  increased. Figure 3 indicates that extrapolated values of  $D_s$  may be nearly equal to  $D_m$  at  $Q_{st} = 0$ , considering the degree of the measurements of  $D_s$  and  $Q_{st}$ . The results in Figure 3 are consistent with those in Figure 2.



**Figure 2.** Ratio of surface diffusion coefficient to molecular diffusivity as a function of adsorption equilibrium constant.



**Figure 3.** Ratio of surface diffusion coefficient to molecular diffusivity as a function of isosteric heat of adsorption. Symbols: see Figure 2.

From the results in Figures 2 and 3, it is concluded that  $D_s$  is probably equal to  $D_m$  when the adsorptive interaction is negligible. Of course, the presence of surface diffusion itself is denied in the absence of the adsorptive interaction. However, the boundary conditions of the presence and absence of surface diffusion are unclear. The change in the features of surface diffusion phenomena seems to be continuous rather than critical because  $K$  and  $Q_{st}$  also continuously change, which represent the intensity of the adsorptive interaction. The results in Figures 2 and 3 suggest that surface diffusion is regarded as a molecular diffusion in a potential field of adsorption restricted due to the adsorptive interaction and should be considered on the basis of molecular diffusion. A formulation of  $D_s$  based on  $D_m$  seems to be possible and is different from eq 3. The mechanism and characteristics of surface diffusion are discussed on the basis of the restricted molecular diffusion model by applying the absolute rate theory.

**Analysis of Molecular Diffusion by the Absolute Rate Theory.** Molecular diffusion in a bulk solvent is regarded as an activated process. Frequently,  $D_m$  is also represented by the Arrhenius type equation

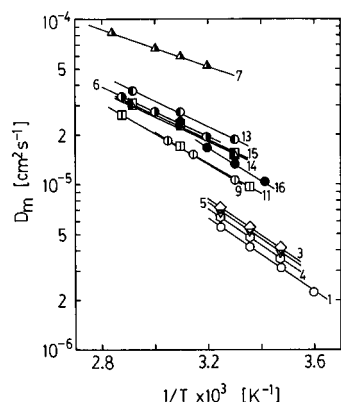
$$D_m = D_{m0} \exp(-E_m/R_g T) \quad (15)$$

where  $D_{m0}$  is a frequency factor and  $E_m$  is an activation energy. On the other hand, according to the absolute rate theory,  $D_m$  is formulated as follows:

$$D_m = (\lambda^2/v_f^{1/3})(kT/2\pi m)^{1/2} \exp(-\alpha \Delta E_v/R_g T) \quad (16)$$

$$v_f^{1/3} = (v/N_A)^{1/3} (CR_g T/\Delta E_v) \quad (17)$$

where  $\lambda$  is the distance between neighboring equilibrium positions,  $v_f$  is the free volume,  $k$  is the Boltzmann constant,  $m$



**Figure 4.** Arrhenius plot of molecular diffusivity. Data numbers: refer to Table 2.

is the molecular weight,  $\alpha$  is a coefficient,  $\Delta E_v$  is the evaporative energy of a solvent,  $v$  is the molecular volume,  $N_A$  is the Avogadro number, and  $C$  is a coefficient. By comparing eqs 15 and 16, the following relationship should be obtained.

$$E_m = \alpha \Delta E_v \quad (18)$$

$$D_{m0} = (\lambda^2 / v_f^{1/3}) (kT / 2\pi m)^{1/2} \quad (19)$$

In Figure 4,  $D_m$  estimated by the Wilke–Chang equation was plotted against  $1/T$ .

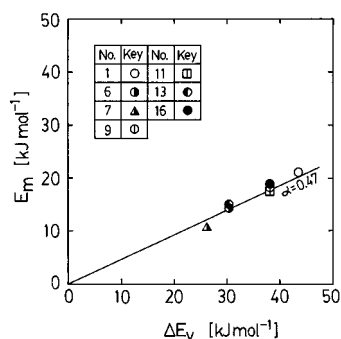
$$D_m = 7.4 \times 10^{-8} (\alpha_a M)^{1/2} T / \eta V_b^{0.6} \quad (20)$$

where  $\alpha_a$  is the association constant,  $M$  is the molar weight,  $\eta$  is the viscosity of a solvent, and  $V_b$  is the molar volume of a solute at normal boiling point. The resulting values of  $E_m$  in eq 15 calculated from the slope of the linear correlations in Figure 4 are listed in Table 2. In Figure 5,  $E_m$  is plotted against  $\Delta E_v$ . The average value of  $\alpha (= E_m / \Delta E_v)$  calculated from the linear correlation in Figure 5 was about 0.47. Similarly, activation energies of viscosity,  $E_{vis}$ , of the various solvents in Table 2 were about 40% of  $\Delta E_v$  of the solvents. Glasstone *et al.*<sup>29</sup> reported that the ratios of  $E_{vis} / \Delta E_v$  ranged from about 0.25 to 0.33. Both values of the ratio of  $E_{vis} / \Delta E_v$  were similar to each other. Because the mechanism of diffusion phenomena is essentially similar to that of viscosity, similar values of  $E_m$  and  $E_{vis}$  should be obtained. The viscosity of a solvent results from the migration of the solvent molecules in the same solvent molecules. On the other hand, in the case of molecular diffusion, a different kind of adsorbate molecules migrate in the solvent molecules. Because the size of adsorbate molecules is usually larger than that of solvent molecules, the generation of larger size of cavity may be required for the migration of adsorbate molecules compared with that of solvent molecules. Slightly larger values of  $E_m$  compared with  $E_{vis}$  may be described to the difference in the size of the cavity for the both types of migration.

According to eq 19,  $D_{m0}$  can be approximated. It was recommended that in the case of molecular diffusion the values of the parameters in eq 16, *i.e.*,  $\lambda$ ,  $v_f^{1/3}$ ,  $\Delta E_v$ , should be calculated from intrinsic values of a solute and solvent by considering the molar fraction of both components. When the concentration of a solute in a solution is low enough, the values of the parameters are almost equal to those of the neat solvent. The values of  $D_{m0}$  estimated for molecular diffusion were ranging from  $3 \times 10^{-3}$  to  $6 \times 10^{-3}$  cm<sup>2</sup> s<sup>-1</sup>, which were almost equal to those for self-diffusion of solvent molecules. On the other hand,  $D_{m0}$  calculated from Arrhenius plots of  $D_m$  estimated by

**TABLE 2: Correlating Results for Experimental Data in This Work and in the Literature**

adsorbate	adsorbent	solvent	$D_{m0}$ (cm <sup>2</sup> s <sup>-1</sup> )	$E_m$ (kJ mol <sup>-1</sup> )	$E_{vis}$ (kJ mol <sup>-1</sup> )	$D_{40}$ (cm <sup>2</sup> s <sup>-1</sup> )	$E_s$ (kJ mol <sup>-1</sup> )	$\Delta E_v$ (kJ mol <sup>-1</sup> )	$\alpha$	$E_{vis} / \Delta E_v$	$-Q_{st}$ (kJ mol <sup>-1</sup> )	$E_s - E_m$ (kJ mol <sup>-1</sup> )	$\beta$	data no.	ref no.
<i>p</i> -tert-octylphenol	ODS-silica gel (45 $\mu$ m)	methanol/water (70/30, vol)	$2.1 \times 10^{-2}$	21.1	18.1	$3.5 \times 10^{-2}$	27.7	43.3	0.49	0.42	16.9	6.6	0.39	1	14
<i>p</i> -tert-octylphenol	ODS-silica gel (24 $\mu$ m)	methanol/water (70/30, vol)	$2.1 \times 10^{-2}$	21.1	18.1	$8.5 \times 10^{-2}$	30.1	43.3	0.49	0.42	16.2	9.0	0.56	2	14
<i>n</i> -butylbenzene	ODS-silica gel (45 $\mu$ m)	methanol/water (70/30, vol)	$2.8 \times 10^{-2}$	21.1	18.1	$3.9 \times 10^{-2}$	25.6	43.3	0.49	0.42	13.0	4.5	0.35	3	this work
<i>n</i> -hexylbenzene	ODS-silica gel (45 $\mu$ m)	methanol/water (70/30, vol)	$2.4 \times 10^{-2}$	21.1	18.1	$7.9 \times 10^{-2}$	28.3	43.3	0.49	0.42	17.5	7.2	0.41	4	this work
anthracene	ODS-silica gel (45 $\mu$ m)	methanol/water (70/30, vol)	$2.7 \times 10^{-2}$	21.1	18.1	$5.4 \times 10^{-2}$	27.1	43.3	0.49	0.42	15.7	6.0	0.38	5	this work
benzene	NaX zeolite (10 $\mu$ m)	cyclohexane	$5.2 \times 10^{-3}$	14.5	12.7	$1.2 \times 10^{-3}$	37.0	30.2	0.48	0.42	24.3	22.5	0.93	6	18
benzene	NaX zeolite (10 $\mu$ m)	<i>n</i> -hexane	$3.1 \times 10^{-3}$	10.6	7.4	$1.2 \times 10^{-3}$	32.7	26.1	0.41	0.28	23.9	22.1	0.92	7	18
benzene	NaX zeolite (20 $\mu$ m)	<i>n</i> -hexane	$3.1 \times 10^{-3}$	10.6	7.4	$3.8 \times 10^{-3}$	35.8	26.1	0.41	0.28	25.1	25.2	1.00	8	18
phenol	Amberlite XAD-7	water	$1.3 \times 10^{-2}$	17.8	16.3	$7.1 \times 10^{-4}$	23.5	38.0	0.47	0.43	23.6	5.7	0.24	9	11, 30
phenol	Amberlite XAD-4	water	$1.3 \times 10^{-2}$	17.8	16.3	$1.1 \times 10^{-1}$	41.6	38.0	0.47	0.43	33.8	23.8	0.70	10	11, 30
benzaldehyde	Amberlite XAD-7	water	$1.1 \times 10^{-2}$	17.5	16.3	$1.4 \times 10^{-1}$	39.8	38.0	0.46	0.43	18.3	22.4	1.22	11	9
benzaldehyde	Amberlite XAD-4	water	$1.1 \times 10^{-2}$	17.5	16.3	$1.1 \times 10^{-3}$	28.8	38.0	0.46	0.43	46.9	11.3	0.24	12	9
acetone	alumina	cyclohexane	$6.5 \times 10^{-3}$	14.7	12.7	$5.1 \times 10^{-3}$	21.6	30.3	0.49	0.42	15	6.9	0.46	13	20
ethylacetate	alumina	cyclohexane	$5.2 \times 10^{-3}$	14.7	12.7	$2.7 \times 10^{-3}$	19.2	30.3	0.49	0.42	16	4.5	0.28	14	20
1-nitropropane	alumina	cyclohexane	$5.3 \times 10^{-3}$	14.7	12.7	$4.6 \times 10^{-4}$	16.6	30.3	0.49	0.42	11	1.9	0.17	15	20
propionic acid	activated carbon	water	$2.4 \times 10^{-2}$	18.9	16.3	$5.2 \times 10^{-1}$	35.0	38.1	0.49	0.43	45.6	16.1	0.35	16	7



**Figure 5.** Correlation of  $E_m$  with  $\Delta E_v$ . Data numbers: refer to Table 2.

eq 20 was ranging from  $3 \times 10^{-3}$  to  $2 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$ . The discrepancy between both  $D_{m0}$  values increased with an increase in the molecular weight of solutes. The difference in the size of solute and solvent molecules seems to influence the accuracy of the estimation of  $D_{m0}$ .

The absolute rate theory is one of the effective strategies for the theoretical analysis of molecular diffusion phenomena. The theory deals with molecular diffusion in liquid phase systems by considering two conceptual processes. One is a hole-making process and the other is a jumping process of a solute from a neighboring site into the hole. An activation energy concerning the hole-making process has been reported to be much larger than that for the jumping one.<sup>11,13,29</sup> The hole-making energy should be almost equal to  $E_m$ , which is approximated as about 47% of  $\Delta E_v$  of a solvent as indicated in Table 2.

**Analysis of Surface Diffusion by the Absolute Rate Theory.** The mechanism of surface diffusion was considered by analyzing experimental data measured or previously published on the basis of the absolute rate theory.

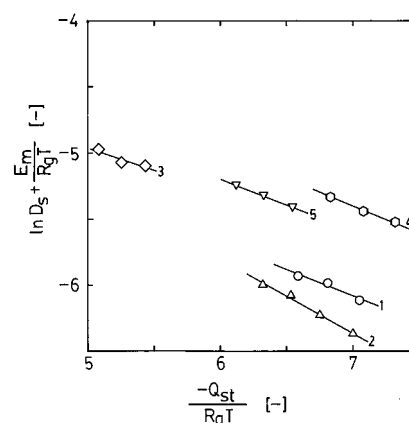
**Activation Energy of Surface Diffusion.** Similarly to a case of molecular diffusion, the mechanism of surface diffusion is assumed to be consist of two hypothetical processes, *i.e.*, a hole-making step and a jumping one. The hole-making step corresponds to the generation of a cavity in solvent molecules presented in the potential field of adsorption at an energetically more stable position, into which an adsorbate molecule can be inserted. The subsequent jumping step may be regarded as the migration of the adsorbate molecule into the next hole by gaining a certain amount of an activation energy and is restrained by the adsorption interaction with an adsorbent.

When solvent molecules are also adsorbed on an adsorbent, the contribution of adsorption potential,  $E_{ap}$ , to the hole-making energy must be considered. Total hole-making energy may be a sum of  $\Delta E_v$  of the solvents and  $E_{ap}$ .  $E_{ap}$  is a free energy required for the transfer of the adsorbable solvents in the potential field of adsorption to a bulk phase and is calculated as follows:

$$E_{ap} = R_g T \ln(c_s/c) \quad (21)$$

where  $c$  and  $c_s$  are the concentration and saturation concentration of an adsorbate in a solvent, respectively. However,  $E_{ap}$  for the adsorbable solvents is probably smaller than  $\Delta E_v$  of the solvents, about 30–40  $\text{kJ mol}^{-1}$  because the concentration of the adsorbable solvents is usually high. On the other hand, when solvent molecules are nonadsorbable, it is unnecessary to consider the influence of the adsorption potential of the solvents on the hole-making energy. It is concluded that  $E_m$  may be regarded as a hole-making energy in the activation process of surface diffusion.

In order to attain the jumping step, it may be enough for an adsorbate molecule to obtain a certain amount of activation



**Figure 6.** Correlation of  $\ln D_s + E_m/R_gT$  with  $-Q_{st}/R_gT$  for reversed-phase liquid chromatographic systems. Data numbers: refer to Table 2.

energy required for surmounting the adsorptive interaction, and for migrating in the potential field of adsorption. Because  $Q_{st}$  is identical to the stabilization energy of the adsorbate molecule, the activation energy for the jumping step may be a fraction of  $-Q_{st}$ . The ratio of the activation energy to  $-Q_{st}$  is expressed as  $\beta$ . By the definition,  $\beta$  takes a positive value smaller than unity. As a result,  $E_s$  is represented as follows:

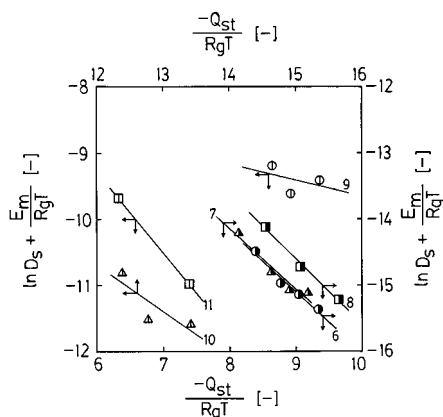
$$E_s = E_m + \beta(-Q_{st}) = \alpha(\Delta E_v) + \beta(-Q_{st}) \quad (22)$$

**Frequency Factor of Surface Diffusion.** The concentration of adsorbate molecules around the surface of an adsorbent increases with proceeding adsorption processes. The molar ratio of the adsorbate molecules to solvent molecules should become large compared with that in the case of molecular diffusion. Under such conditions, the parameters  $\lambda$ ,  $v_f$ , and  $\Delta E_v$  should be estimated from the physical properties of neat adsorbate and solvent by taking into account the molar fraction of both components when  $D_{s0}$  is calculated by eqs 17 and 19. The molar fraction in the immediate neighborhood of the surface, however, cannot be accurately determined. It is also presumed that physical properties of both components in a potential field of adsorption differ from those under unrestricted state. For example, solvent structure neighboring to the surface of an adsorbent may be different from that in a bulk phase, suggesting that the values of  $\lambda$ ,  $v_f$ , and  $C$  may be changed. On the other hand, adsorbate molecules must also be restrained on the surface of an adsorbent by an adsorption potential. The evaporative energy of the adsorbate molecules adsorbed is larger than that in the absence of adsorbents. The value of  $v_f$  must be reduced. In conclusion, strict calculations cannot be performed for  $D_{s0}$  at present time. However, it is expected that the parameters in eq 16 are almost constant in a narrow temperature range for each adsorption system. Temperature change provides no serious influence on  $D_{s0}$  because it is only proportional to  $T^{-1/2}$  as indicated in eqs 17 and 19. Quantitative analysis of  $E_s$  can be made by assuming that  $D_{s0}$  is independent of temperature in a narrow temperature range.

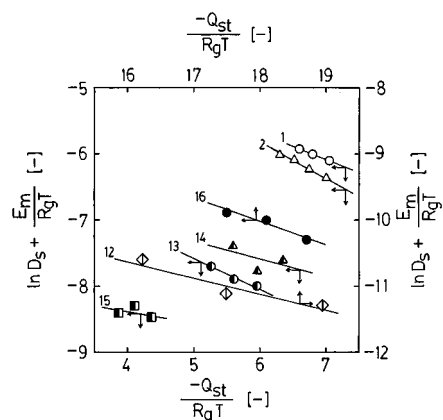
**Analysis of Temperature Dependence of  $D_s$ .** Surface diffusion is usually regarded as an activated process. By substituting eq 22 into eq 1, the following equation is derived.

$$D_s = D_{s0} \exp[-(E_m + \beta(-Q_{st}))/R_gT] \quad (23)$$

According to eq 23,  $\ln D_s + E_m/R_gT$  is plotted against  $-Q_{st}/R_gT$  in Figures 6–8. The values of  $\beta$  were determined from the slope of the linear correlations in Figures 6–8. As shown in Table 2,  $\beta$  was usually ranging from about 0.2 to 0.5,



**Figure 7.** Correlation of  $\ln D_s + E_m/R_gT$  with  $-Q_{st}/R_gT$  for liquid phase adsorption systems. Data numbers: refer to Table 2.



**Figure 8.** Correlation of  $\ln D_s + E_m/R_gT$  with  $-Q_{st}/R_gT$  for liquid phase adsorption systems. Data numbers: refer to Table 2.

indicating that adsorbate molecules must obtain an activation energy equal to about from one fifth to half of  $(-Q_{st})$  in order to overcome the adsorptive interaction and to jump into a next hole. These values are in agreement with those for the surface diffusion in gaseous adsorption. When adsorbate molecules diffuse in micropores filled with a solvent, larger values of  $\beta$ , namely nearly equal to unity, were also observed even in liquid phase adsorption. The value of  $\beta$  is probably dependent on the size of pore in adsorbents. Large values of  $E_s$  nearly equal to or larger than  $-Q_{st}$  were also reported for the micropore diffusion in gaseous systems. On the other hand,  $D_{s0}$  is calculated from the intercept of the linear correlations in Figures 6–8. As listed in Table 2, the  $D_{s0}$  and  $D_{m0}$  calculated are of the same order of magnitude in many cases though complete agreement is not attained. Similar values of  $D_{s0}$  were experimentally observed for various adsorbates in previous papers.<sup>15,16,22</sup> The discrepancy between  $D_{s0}$  and  $D_{m0}$  may be partially caused by the influence of the adsorption potential due to the presence of adsorbents as described above. In addition, experimental errors in the determination of  $D_{s0}$  probably provide an influence on the discrepancy. For example, in the case that  $D_s$  is  $1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  at 298 K,  $D_{s0}$  is calculated as  $3.2 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$  when  $E_s$  is assumed to be  $20 \text{ kJ mol}^{-1}$ . Similarly, when  $E_s$  is  $21 \text{ kJ mol}^{-1}$ ,  $D_{s0}$  is calculated as  $4.8 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$ . The difference in  $E_s$  in an error of 5% corresponds to that in  $D_{s0}$  of about 50%. The hypothetical calculation indicates that accurate determination of  $D_{s0}$  is quite difficult. Especially, a remarkable scatter was observed in aqueous adsorption systems, suggesting that the influence of the change in chemical properties and structure of water molecules on molecular diffusion must be considered when  $D_{s0}$  is quantitatively analyzed. Further progress of basic studies relating to the

properties and structures of solvents is essential. The trends of the significantly scattering data for macromolecular hydrophobic resins, XAD-4 and XAD-7, cannot be explained in terms of only hydrophobicity. Accumulation of more accurate measurements of experimental data of surface diffusion is surely essential for the elucidation of the migration mechanism of adsorbate molecules on the surface of adsorbents in further detail.

In this paper, the correlation between  $D_s$  and the intensity of the adsorptive interaction was studied by changing the chain length of alkyl ligands bonded on the surface of silica gel. The change in the alkyl chain length brings about the variation in hydrophobicity of adsorbents. The situation of neighbor solvent molecules may be simultaneously changed. Though the influence of the chemical modification of the surface of silica gel on  $D_{s0}$  cannot be exactly evaluated at the present time, an attempt was made to correlate  $D_s$  with the magnitude of the adsorptive interaction by assuming that the parameters in eq 16 are constant irrespective of the alkyl chain length. The following equation is derived from eqs 15 and 23.

$$\ln(D_s/D_m) = \ln(D_{s0}/D_{m0}) - \beta(-Q_{st})/R_gT \quad (24)$$

Equation 24 suggests the presence of a linear correlation between  $\ln(D_s/D_m)$  and  $-Q_{st}$  as shown in Figure 3. The almost linear profile of experimental data in Figure 3 proves the validity of eq 24. From the slope of the linear plots in Figure 6,  $\beta$  was experimentally determined as about 0.4 for reversed-phase liquid chromatographic systems using ODS–silica gel as an adsorbent. Figure 3 postulates a simulated correlation (dotted line) between  $\ln(D_s/D_m)$  and  $-Q_{st}$  calculated by taking  $\beta$  as 0.4 and by assuming  $D_{s0} = D_{m0}$ , which is almost parallel with experimental data. However, the experimental data were larger than the simulated line by a factor of about 2–3. The discrepancy between the experimental plots and calculated values of  $D_s/D_m$  may be resulting from the error in the estimation of the frequency factors, *i.e.*,  $D_{s0}$  and  $D_{m0}$ . Figure 2 illustrates the correlation (dotted line) between  $D_s/D_m$  and  $K$  estimated on the basis of the dotted line in Figure 3. The values of  $D_s/D_m$  for several data in Figure 3 were plotted according to  $K$  in Figure 2. The temperature dependence of  $K$  has been usually represented by the van't Hoff equation

$$K = K_0 \exp(-Q_{st}/R_gT) \quad (25)$$

where  $K_0$  is  $K$  at  $1/T = 0$  or  $Q_{st} = 0$ . By combining eqs 24 and 25

$$D_s/D_m = (D_{s0}/D_{m0})(K_0/K)^\beta = (D_{s0}/D_{m0})[\exp(Q_{st}/R_gT)]^\beta \quad (26)$$

Equation 26 indicates that the ratio of  $D_s/D_m$  is inversely proportional to  $K$  as shown in Figure 2. The results in Figures 2 and 3 indicate that  $D_s$  can be approximated according to the intensity of the adsorptive interaction even under the conditions that  $K$  or  $Q_{st}$  is quite small.

Similarly to eq 22, a linear relation between  $E_s$  and  $Q_{st}$  was suggested by Itaya *et al.*<sup>11</sup> and Komiyama and Smith.<sup>9,10</sup> The terms of  $E_m$  and  $\beta(-Q_{st})$  correspond to a hole-making step and jumping one, respectively. The generation of the hole probably results from the movement of solvent molecules, not of adsorbate molecules. Itaya *et al.*<sup>11</sup> correlated  $D_s$  to  $Q_{st}$  and indicated linear correlations between  $\ln D_s$  and  $-Q_{st}/R_gT$ . From quantitative analysis of the linear correlations, they reported that  $\beta$  was ranging from about 0.3 to 0.6, which is sufficiently in agreement with the results listed in Table 2. Itaya *et al.* reported that  $E_m$  for Amberlite XAD-4 was larger than that for XAD-7.

They concluded that the larger  $E_m$  for XAD-4 compared with that for XAD-7 could not be interpreted because XAD-7 was more hydrophilic than XAD-4, and solvent (water) molecules should be more adsorbed on XAD-7 rather than XAD-4. However, when polar solvent molecules contact with a hydrophobic surface, mutual repulsion appears between the solvent molecules and the surface. The polar solvent molecules may be compressed by the structure-making effect. In such cases, the interaction between the polar solvent molecules may be amplified and the parameters, *i.e.*,  $v_f$  and  $C$ , may also change. The larger  $E_m$  for the more hydrophobic adsorbent XAD-4 is probably caused by the influence of the solvent structure-making effect. According to the absolute rate theory,  $E_m$  is regarded as an activation energy for a hole-making step and is correlated with  $\Delta E_v$  of a solvent. Solvent structure-making is accelerated when solvent molecules are significantly attracted on the surface of adsorbents or repulsed from the surface. In such cases, larger values of  $E_m$  may be expected. On the contrary, relatively small  $E_m$  is probably observed when solvent structure is destroyed by the interaction between solvent molecules and the surface of adsorbents. By correlating  $Q_{st}$  with an activation energy for the jumping step, the influence of the adsorptive interaction between adsorbate molecules and adsorbents on surface diffusion was taken into account in this model.

**An Interpretation of Various Correlations between  $E_s$  and  $Q_{st}$ .** In many cases of liquid phase adsorption,<sup>14-16,18-23</sup>  $E_s$  has been found to be larger than  $-Q_{st}$ , suggesting that the surface migration of an adsorbate molecule requires larger activation energy compared with a complete desorption of the adsorbate molecule from a surface to a bulk solvent phase. This thermodynamic situation suggests a negative conclusion relating to the presence of surface diffusion phenomena. On the contrary,  $E_s$  smaller than  $-Q_{st}$  has also been reported even in liquid phase adsorption.<sup>7,24</sup> In gas phase adsorption, the ratios of  $E_s/-Q_{st}$  were usually ranging from about 0.3 to 1 for surface diffusion.<sup>1-4,27</sup> The values of  $E_s/-Q_{st}$  larger than unity have also been reported for gaseous micropore diffusion. An attempt was made to explain the various situations of the correlation between  $E_s$  and  $Q_{st}$  in liquid phase adsorption according to eqs 22 and 23.

It is assumed that  $E_s$  consists of the contributions of both a hole-making step and a jumping step. The activation energy of the hole-making step may be proportional to  $\Delta E_v$  of a solvent, not of an adsorbate. An average value of  $\alpha$  was about 0.47, whereas Glasstone *et al.*<sup>29</sup> reported corresponding values of about 0.25–0.33 for viscosity of solvents. Because  $\Delta E_v$  of various solvents, such as water, alcohols, and aromatic hydrocarbons, are ranging from about 30 to 40 kJ mol<sup>-1</sup>, the contribution of the hole-making step is calculated to be about 15–20 kJ mol<sup>-1</sup>. Similarly, the contribution of the jumping step may be correlated with  $Q_{st}$  of an adsorbate. The average value of  $\beta$  was about 0.4 for surface diffusion in liquid phase adsorption. When  $Q_{st}$  is  $-20$  kJ mol<sup>-1</sup>, the contribution of the jumping step is approximated as about 8 kJ mol<sup>-1</sup>. Totally,  $E_s$  is calculated as about 23–28 kJ mol<sup>-1</sup>. In such a case  $E_s$  should be larger than  $-Q_{st}$ . In contrast, when  $Q_{st}$  is  $-50$  kJ mol<sup>-1</sup>, the activation energy of the jumping step is estimated as about 20 kJ mol<sup>-1</sup>, and total  $E_s$  is about 35–40 kJ mol<sup>-1</sup>. In such a case, the ratio of  $E_s/-Q_{st}$  should be smaller than unity. Phenomenally, when the value of 0.6 times  $-Q_{st}$  is larger than the activation energy of the formation of a hole, *i.e.*, about 15–20 kJ mol<sup>-1</sup>,  $E_s$  should be smaller than  $-Q_{st}$ . It corresponds to the conditions that the absolute value of  $Q_{st}$  is larger than about 35 kJ mol<sup>-1</sup>. This hypothesis is supported by experimental data previously published, in which  $-Q_{st}$  was larger than about 40 kJ

mol<sup>-1</sup>.<sup>9,11</sup> The various thermodynamic correlations between  $E_s$  and  $Q_{st}$  in liquid phase adsorption were interpreted on the basis of the restricted molecular diffusion model.

## Conclusion

Surface diffusion phenomena in reversed-phase liquid chromatography were analyzed by considering the adsorptive interaction of adsorbate molecules with adsorbents. The correlation between surface and molecular diffusions of adsorbates was indicated. A restricted molecular diffusion model was proposed as one approximation of the mechanism of surface diffusion. The formulation of  $D_s$  based on  $D_m$  was derived according to the absolute rate theory. It was assumed that  $E_s$  was represented as the sum of the two contributions, *i.e.*, a hole-making step and a jumping one. The contribution of the hole-making step was correlated with  $\Delta E_v$  of a solvent, not of an adsorbate. The contribution of the jumping step was considered as a certain fraction of  $-Q_{st}$ . Though the accuracy of the estimation of  $D_{s0}$  was not sufficient, characteristic features of  $E_s$  could be adequately interpreted by the model. An explanation was provided for the various correlations between  $E_s$  and  $Q_{st}$  in liquid phase systems, namely  $E_s$  was larger than, almost equal to, or smaller than  $-Q_{st}$ . The equation proposed represents the dependence of  $D_s$  on both temperature and the adsorbability of adsorbates.

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