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Estimation of the Surface-Diffusion Coefficient in Gas-Phase Adsorption Using Octadecylsilyl-Silica Gel

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Surface-diffusion data in a gaseous adsorption system using an octadecylsilyl-silica gel as an adsorbent were analyzed according to a restricted Knudsen diffusion model. A linear correlation was confirmed between the ratio of the restriction energy for Knudsen diffusion to the isosteric heat of adsorption, Q_{st}, and $1/(-Q_{st})$. It was proved that a linear correlation could be observed under the conditions that a linear free-energy relation and an enthalpy–entropy compensation in adsorption equilibrium were established. An estimation procedure of the surface-diffusion coefficient (D_s) was proposed based on the results. It was demonstrated that D_s of various adsorbates at given temperatures could be estimated with an error of less than about 50% from only one datum of the adsorption equilibrium constant measured at a different temperature. Similarly, D_s in gas-phase adsorption could be estimated from the evaporative energy of the adsorbates without experimental data.

It is well known that in many cases of gas-phase adsorption, surface diffusion plays an important role for intraparticle diffusion in porous materials.[1,2] The surface-diffusion coefficient (D_s) has been usually formulated as

$$D_s = D_{s0}\exp(-E_s/R_gT) = D_{s0}\exp[-\alpha(-Q_{st})/R_gT], \qquad (1)$$

where D_{s0} and E_s denote the frequency factor and the activation energy of surface diffusion, respectively. Q_{st} denotes the isosteric heat of adsorption. R_g and T are the gas constant and the temperature. The characteristic features and migration mechanism of surface diffusion have been discussed based on the ordinary equation. Quantitative studies have also been carried out on the physical meanings of the parameters in Eq. 1. E_s is correlated with Q_{st} by introducing an empirical coefficient (α). The dependence of D_s on an adsorbed amount (q) has been interpreted by considering the change in Q_{st} resulting from a change in q.[3] The values of α are experimentally found to be less than unity in surface diffusion. Mitani et al. confirmed linear correlations between the logarithms of the Henry constant and D_s for various gas-phase adsorption systems.[4] It was indicated from the slope of the linear correlations that α ranged from about 0.3 to 1.0. Okazaki et al. provided an interpretation of the physical meaning of D_{s0} based on a hopping model, and proposed an estimation procedure of D_{s0}.[5] They improved a random hopping model for surface diffusion by considering the average holding times of molecules adsorbed in a monolayer and multilayers separately, and explained the dependence of D_s on q and the temperature by applying the model.[5]

Contrary to extensive studies concerning the characteristics and mechanism of surface diffusion, a very few procedures have been proposed for estimating D_s. It may be hard to accurately estimate D_s, because it significantly varies with the combination of adsorbates and adsorbents. Surface-diffusion phenomena are probably influenced by their physical properties, such as the size, shape, and magnitude of the adsorptive interaction between them. Sladek et al. correlated many experimental data over a wide range from physisorption to chemisorption by a single straight line according to Eq. 1.[6] A linear correlation can be used only for estimating the order of D_s from Q_s. Tamon et al. proposed a prediction procedure of D_s based on the random hopping model.[7] The value of D_{s0} was correlated with a specific surface area by using two empirical parameters, the values of which were determined from previously published experimental data. Though the method of Tamon et al. is complicated, a more accurate estimation of D_s seems to be possible compared with that proposed by Sladek et al. A convenient procedure for estimating D_s should be derived in connection with a more detailed understanding of surface-diffusion phenomena.

This paper is concerned with an estimation of D_s in gas-phase adsorption using a hydrophobic adsorbent according to a restricted Knudsen diffusion model. An octadecylsilyl (ODS)-silica gel was used as an adsorbent. The characteristic features of some parameters in the model were clarified by considering a few correlations in gas-phase adsorption, i.e., a linear free-energy relation (LFER) and an enthalpy–entropy compensation effect in adsorption equilibrium. An estimation procedure of D_s has been proposed based on the results.

Theory

As previously pointed out,[3,8] the adsorptive interaction between adsorbates and adsorbents restricts the migration of adsorbate molecules on a surface in both gas- and liquid-phase system. Equation 1 explains this situation and indicates that D_s is almost equal to D_{s0} under the limiting condition that Q_{st} is negligibly small. In the hopping model D_{s0} is represented as

$$D_{s0} = C\lambda^2\tau, \tag{2}$$

where C, λ, and τ denote the constant, depending on the properties of the adsorbent, the mean free path, and the jump frequency, respectively. It was attempted to explain the dependence of D_s on q by considering the concentration dependence of λ and τ. As indicated in Eq. 2, the characteristics of D_{s0} have been interpreted by assuming the hopping migration of adsorbate molecules on the surface of adsorbents. This explanation of D_{s0} is unrelated to the mechanism of Knudsen diffusion. However, the mechanism of surface diffusion seems to approach that of nonadsorbable molecules, i.e., Knudsen diffusion, with a decrease in the absolute value of Q_{st}. The mass-transfer mechanism of nonadsorbable gases in micro- and meso-pores usually obeys that of Knudsen diffusion. The presence of surface-diffusion phenomena is expected only when adsorbate molecules are adsorbed on the surface of adsorbents. The difference between surface diffusion and Knudsen diffusion is attributed to the presence and absence of an adsorptive interaction. It may be strange that the mass-transfer mechanism critically changes between the entirely different manners, i.e., hopping migration and Knudsen diffusion, under certain conditions in spite of the continuous change in the adsorptive interaction represented by Q_{st}. Equation 1 provides no information with respect to this subject. The development of a different formula regarding D_s must be required in order to specify the mechanism of surface diffusion in more detail.

In this study, it is assumed that surface diffusion is a mass-transfer phenomenon of an adsorbate molecule in a potential field of adsorption in a neighbor region of the surface of an adsorbent. In order to migrate in the region, the adsorptive interaction between the adsorbate molecule and the adsorbent must be broken and the adsorbate molecule must be released from the surface. The process may be an activated type. It is required for the adsorbate molecule to obtain a certain activation energy in order to overcome the adsorptive interaction. The adsorbate molecule separated from the surface probably migrates to another adsorption site in a similar manner to Knudsen diffusion. However, the adsorbate molecule does not go out from the potential field of adsorption because the adsorbate molecule is not completely desorbed. A continuous change in D_s, due to a change in the strength of the adsorptive interaction, can be explained irrespective of the value of Q_{st} when the surface-diffusion mechanism is assumed to be the restricted Knudsen diffusion described above.

The mechanism of surface diffusion is considered by taking into account the correlation between surface and Knudsen diffusions. According to the kinetic theory of gases, the average velocity of molecules (v) is

$$v = (8R_gT/\pi M)^{1/2}, \tag{3}$$

where M is the molecular weight. A definition of diffusivity (D) is represented as

$$D = (1/3)\lambda v. \tag{4}$$

The value of λ is equal to the pore diameter ($2r_p$) under the conditions that the total pressure is low or the pore diameter is sufficiently small. In such a case, D corresponds to the Knudsen diffusivity (D_k) and is calculated by the following ordinary equation for the Knudsen diffusion.[9]

$$D_k = (1/3)(2r_p)v = (2/3)r_p(8R_gT/\pi M)^{1/2}. \tag{5}$$

The knudsen diffusivity of nonadsorbable molecules can be estimated by Eq. 5

On the other hand, for adsorbate molecules, a gain in the activation energy (E_r) is required to overcome any restriction due to the adsorptive interaction, and to migrate in the neighbor region of the surface. However, it is unnecessary that E_r be beyond the absolute value of Q_{st}, because it is not necessary for adsorbate molecules to be completely desorbed to a bulk phase. The value of E_r should be a certain fraction of $-Q_{st}$, because the strength of the adsorptive interaction can be represented by Q_{st}.[10] The ratio of $E_r/(-Q_{st})$, which is called γ, should be positive and smaller than unity. Similar consideractions of the entirely empirical parameter (α) in Eq. 1 have been sufficiently confirmed for surface-diffusion phenomena in many gas-phase adsorption systems.[1—3] The value of D_s is hypothetically represented as follows by assuming surface diffusion as mass-transfer phenomena in the potential field of adsorption,

$$D_s = D_k \exp(-E_r/R_gT) = D_k \exp(-\gamma(-Q_{st}/R_gT), \tag{6}$$

where E_r is the restriction energy for diffusion. Equation 6 is derived based on the assumption that the surface diffusion be regarded as Knudsen diffusion restricted by the adsorptive interaction. Equation 6 indicates that molecules adsorbed on a surface can be partially desorbed and migrate in the manner of the Knudsen diffusion when the molecules obtain an activation energy larger than $\gamma(-Q_{st})$. Because D_k can be numerically estimated, D_s can be calculated according to Eq. 6 if the values of γ and Q_{st} are known.

Experimental

Apparatus: Pulse-response experiments in a gaseous system were carried out on a gas chromatograph (GC-9A, Shimadzu). A gas-tight syringe was used to inject the adsorbate gas into a carrier flow. The flow rate of the carrier gas, helium, was determined by a soap-film flowmeter at the outlet of a thermal conductivity detector, by which the concentration of the adsorbates in the effluent was monitored. The column temperature was kept constant by using a thermostatted methanol–water mixture bath or a conventional column oven for the gas chromatograph.

ODS Column and Reagents: In this study, an ODS-silica gel was used as a hydrophobic adsorbent. ODS-silica gel adsorbents are the most popular in reversed-phase liquid chromatography (RP-LC). They are also used as packing materials in gas chromatography. A commercial product has already been provided by a manufacturer. The authors have made some fundamental studies on the adsorption characteristics in RP-LC. The influence of a solvent on an interaction between adsorbate molecules and the surface of the adsorbents is one of the most important subjects to elucidate the separation mechanism in RP-LC. A corresponding study in a gaseous system using ODS-silica gel was made as a reference.[11] Table 1 gives the properties of the ODS-silica gel particles (YMC). The average particle diameter of the packing materials was determined by a scanning electron microscope. The ODS-silica gel was chemically synthesized by reacting a silane coupling reagent, dimethyloctadecylchlorosilane, with an amorphous silica-gel support. The functionality of the ODS ligand may be monomeric. The carbon content was 19.8 wt%., suggesting that the ODS ligand density seemed to be about 1.5 nm^{-1}, because the specific surface area of the silica-gel support was about 450 $\mathrm{m}^2\,\mathrm{g}^{-1}$. It is indicated that about 30% of the silanol groups on the surface of the silica-gel support is reacted with the silane coupling reagent, because the density of silanol groups on the surface of silica-gel is reported to be about 8 $\mu\mathrm{mol\,m}^{-2}$. This figure may be close to a typical value, which can be achieved by chemical bonding of the ODS ligands onto the surface of the silica-gel. It has been reported that the ODS ligand density ranges from about 2.4 to 2.9 $\mu\mathrm{mol\,m}^{-2}$, because of the steric hindrance of the ODS ligands when the ODS silane coupling reagent is used. The value of the ODS ligand density about 1.5 nm^{-1}, suggesting that monomeric ODS ligands (about 2.45 nm in length) are placed at intervals of about 0.8 nm on the surface of the ODS-silica-gel particles. It is unclear whether the ODS ligands are extended or not. Sample organic substances are probably adsorbed on the ODS ligands by means of a hydrophobic interaction. As listed in Table 1, the pore radius is calculated to be about 4.86 nm from the values of the pore volume and specific surface area by assuming a cylindrical pore shape. The tortuosity factor of the pores was determined from liquid-chromatographic experiments using uracil as an inert substance. The thermostability of the adsorbent was confirmed on the basis of a thermal gravity analysis. Slight decreases in the weight and exothermal phenomenon were observed at a temperature of about 450 K, or above. The upper limit of the experimental temperature was determined to be 418 K by taking into account the thermostability of the ODS-silica-gel. An ODS column was prepared by packing the adsorbent particles into a glass column. The purity of helium was 99.9%. Several nonpolar organic compounds, such as alkanes and benzene derivatives, were used. The boiling points of the adsorbates were lower than about 410 K.

Table 1. Properties of ODS Column and Experimental Conditions

Column	ODS
Av. particle diam. (μm)	296
Particle density ($\mathrm{g\,cm}^{-3}$)	0.95
Porosity (—)	0.37
Pore volume ($\mathrm{cm}^3\,\mathrm{g}^{-1}$)	0.39
Pore radius, r_p (nm)	4.86
Specific surface area ($\mathrm{m}^2\,\mathrm{g}^{-1}$)	162
Carbon content (wt%)	19.8
Mass of adsorbent (g)	1.03
Column size (mm)	3.2 ID × 195
Void fraction (—)	0.31
Tortuosity factor (—)	8.4
Column temperature (K)	260—418
Carrier gas	Helium
Volumetric flow rate ($\mathrm{cm}^3\,\mathrm{s}^{-1}$)	0.5—1.0
Superficial velocity ($\mathrm{cm\,s}^{-1}$)	7.1—14.1
Sample materials	Benzene derivatives, Alkanes

Procedure: The experimental conditions are also listed in Table 1. Pulse-response experiments were made at zero surface coverage of the adsorbates while varying both the column temperature and the flow rate of the carrier gas. Small pulses of the adsorbate gas were introduced into the carrier gas flow at the inlet of the ODS column.

Data Analysis: Chromatographic peaks were analyzed by the method of moments.[2] The details concerning the moment analysis have been described in previous papers.[11,12] Information about the adsorption equilibrium and mass-transfer rates in the column was obtained from the first and second moments, μ_1 and μ_2', respectively. In this study, the D_s values were determined from μ_2' by correcting the effect of a few mass-transfer steps on peak spreading. Some parameters, i.e., D_k, fluid-to-particle mass-transfer coefficient (k_f), and pore diffusivity (D_p) are correlated with the mass-transfer rates. The uncertainty in estimating the parameters influences the determination of D_s. The value of D_k was calculated by Eq. 5. The accuracy in estimating D_k must be considered. However, the authors have heard nothing yet about the estimation error of D_k. With respect to the molecular diffusivity (D_m) in gaseous systems, various correlations have also been proposed.[9,13] An average error of about 5—10% was reported for estimating D_m by the correlations.

The intraparticle diffusivity (D_e) was determined from μ_2' by subtracting the contribution of fluid-to-particle mass transfer to peak spreading. The value of k_f was estimated by the Carberry equation. However, the uncertainty in the estimation of k_f provides little influence on the determination of D_s. The contribution of the fluid-to-particle mass-transfer resistance was found to be about 1 or 2 orders of magnitude smaller than those of the axial dispersion and intraparticle diffusion in gaseous systems.[11]

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_k according to the parallel-pore model. In such a case, the uncertainty in the estimation of D_p corresponds to that of D_k. As previously indicated,[11] the contribution of surface diffusion to the overall mass transfer in ODS-silica-gel particles is as much as about 45—85%, or above. Because surface diffusion plays a dominant role for intraparticle diffusion in most cases, the influence of the variation in the estimation of D_p on the determination of D_s can be neglected. Based on the consideration described above, it is concluded that the values of D_s are probably obtained with an error of about several per cent.

Results and Discussion

Correlation between E_r and Q_st: Figure 1 illustrates the correlation between E_r and Q_st. According to Eq. 6, the E_r values listed in Table 2 were calculated from the experimentally determined D_s and D_k estimated at each intermediate temperature. The temperature dependence of the adsorption equilibrium constant (K) determined from μ_1, was analyzed by the van't Hoff equation,

$$K = K_0 \exp(-Q_\mathrm{st}/R_\mathrm{g}T), \tag{7}$$

where K_0 is K at $1/T=0$. The values of Q_st and K_0 were calculated from the slope and intercept of linear relationships between $\ln K$ and $1/T$, respectively. The average value of γ is about 0.52 for all plots in Fig. 1. An approximate estimation of D_s is probably possible by taking γ as 0.52. However, the values of E_r are almost constant, irrespective of Q_st. The

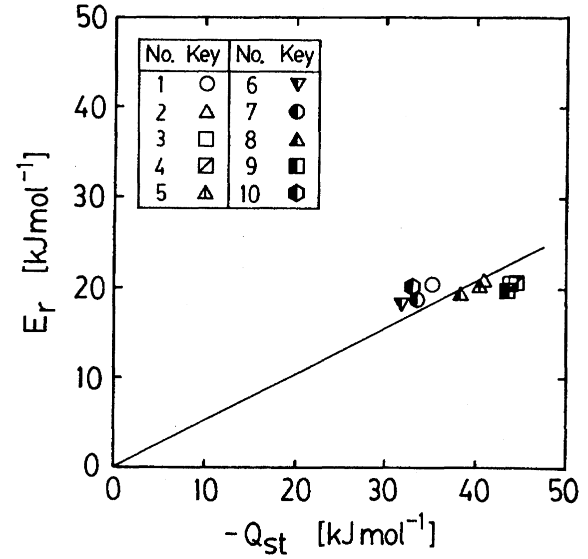

Fig. 1. Correlation between E_r and Q_{st}. Data numbers: refer to Table 2.

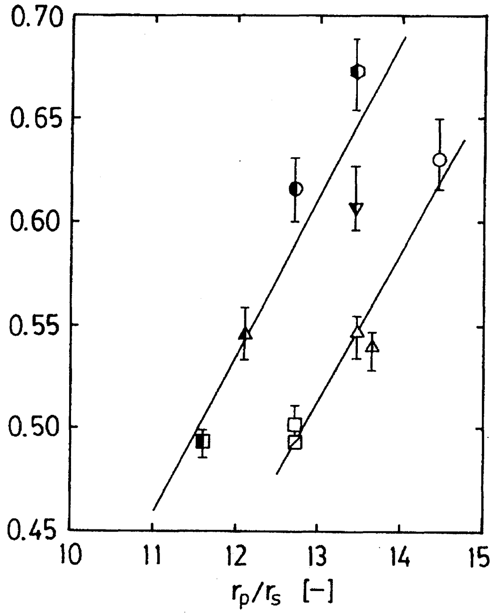

Fig. 2. Correlation between γ and r_p/r_s. Symbols: refer to Fig. 1 and Table 2.

magnitude of the change in E_r is quite small compared with that in Q_{st}. The ratio $E_r/(-Q_{st})$ is not constant. The physical meaning of γ must be specified in more detail in order to accurately estimate D_s.

Correlation of γ with Some Parameters: Satterfield et al. reported on the concept of a restricted diffusion of solutes in liquid-phase adsorption.[8] The migration of the solutes in fine pores was restricted due to both a hydrodynamic effect and the adsorptive interaction between adsorbates and adsorbents. However, they did not make a detailed analysis of surface diffusion in both gas- and liquid-phase adsorption based on the restricted diffusion model. They indicated that the logarithm of the ratio of the effective diffusivity of solutes in pores to the bulk diffusivity decreased linearly with increasing ratio of the the solute molecular diameter to the pore diameter. The correlation of γ with the ratio of the pore radius (r_p) to the radius of the adsorbate molecules (r_s) is similarly shown in Fig. 2. The values of r_s were calculated from the molecular volume at the normal boiling point of each adsorbate. In contradiction to the results of Satterfield et al.,[8] γ increases along with an increase in r_p/r_s, even in a narrow range of r_p/r_s from 11 to 15. It is preferable to estimate γ from only the information about the size of pores and adsorbates. However, it may be hard to explain that γ is larger in wide pores than in narrow pores.

Similarly, Fig. 3 represents the correlation of Q_{st} with r_p/r_s. In contrast with the results in Fig. 2, $-Q_{st}$ decreases along with an increase in r_p/r_s. The different linear correlations were observed for each homology. In gaseous adsorption on a surface, the ratio of $-Q_{st}$ to the heat of vaporization (ΔH_v) is reported to be about 1.2—1.6. On the other hand, the ratio $(-Q_{st})/\Delta H_v$ is found to be between 2 and 3 for microporous adsorbents, such as molecular sieving carbons and zeolites.[2] An adsorptive interaction between adsorbate molecules and

Table 2. Correlating Results for Experimental Data

Adsorbate	Adsorbent	r_p nm	T K	E_r kJ mol^{-1}	$-Q_{st}$ kJ mol^{-1}	r_p/r_s	γ	ΔH_v kJ mol^{-1}	$(-Q_{st})/\Delta H_v$	Data number
Benzene	ODS-silica gel	4.86	323—373	19.9—21.1 (20.4)[a]	35.3	14.4	0.61—0.65 (0.63)[a]	31.7	1.11	1
Toluene	ODS-silica gel	4.86	343—403	20.0—20.8 (20.5)	40.7	13.5	0.53—0.55 (0.55)	33.5	1.21	2
Ethylbenzene	ODS-silica gel	4.86	388—418	20.1—20.7 (20.4)	43.8	12.7	0.50—0.51 (0.50)	33.5	1.31	3
p-Xylene	ODS-silica gel	4.86	368—423	20.2—20.8 (20.4)	44.6	12.7	0.49—0.50 (0.49)	36.1	1.24	4
Chlorobenzene	ODS-silica gel	4.86	363—413	19.7—20.4 (20.1)	40.5	13.6	0.53—0.55 (0.54)	37.2	1.09	5
Pentane	ODS-silica gel	4.86	283—313	17.9—18.9 (18.3)	31.7	13.5	0.60—0.63 (0.61)	25.8	1.23	6
Hexane	ODS-silica gel	4.86	313—363	18.4—19.3 (18.8)	33.4	12.7	0.60—0.63 (0.62)	28.85	1.16	7
Heptane	ODS-silica gel	4.86	333—383	18.8—19.7 (19.2)	38.2	12.1	0.53—0.56 (0.55)	31.69	1.21	8
Octane	ODS-silica gel	4.86	368—408	19.5—20.1 (19.8)	43.4	11.6	0.48—0.50 (0.49)	35.0	1.24	9
Cyclohexane	ODS-silica gel	4.86	313—373	19.6—20.6 (20.1)	33.0	13.5	0.65—0.69 (0.67)	33.0	1.00	10
Ethane	ODS-silica gel	4.86	260—293	—	14.7	—	—	14.72	1.00	—
Propane	ODS-silica gel	4.86	260—293	—	22.3	—	—	18.77	1.19	—
Butane	ODS-silica gel	4.86	260—303	—	26.4	—	—	21.29	1.24	—

a) The numbers in parentheses are average values.

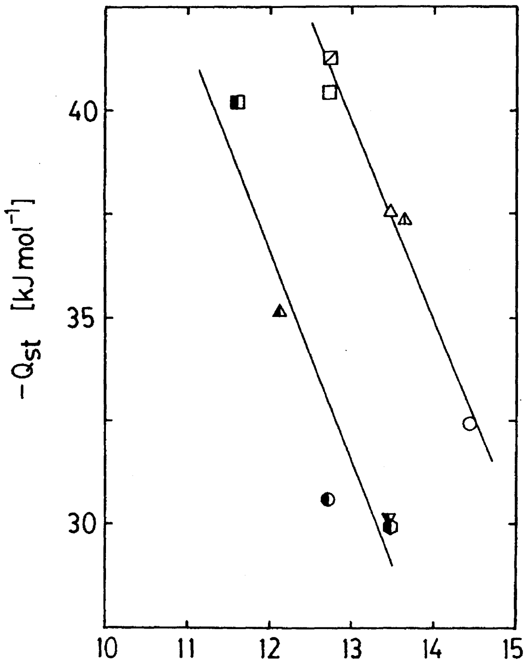

Fig. 3. Correlation between Q_{st} and r_p/r_s. Symbols: refer to Fig. 1 and Table 2.

the pore wall of the adsorbents is probably amplified when the molecular size of the adsorbates is comparable to that of the pores. The plots in Fig. 3 also indicate similar results in the correlation between Q_{st} and r_p/r_s.

Figure 4 illustrates a linear correlation between γ and $1/(-Q_{st})$, which is calculated by combining the results in Figs. 2 and 3. The plots are the average values of γ measured over each temperature range of about 50—60 K, as indicated in Table 2. The magnitude of scatter in γ was about 0.01—0.03, suggesting that the temperature dependence of γ is small. Even though γ varies over the range, D_s hypothetically calculated at 350 K is probably estimated with an error of about 50% under the intermediate experimental conditions that Q_{st} is -35 kJ mol^{-1}. It is concluded that the effect of temperature on the estimation of D_s is not extremely serious.

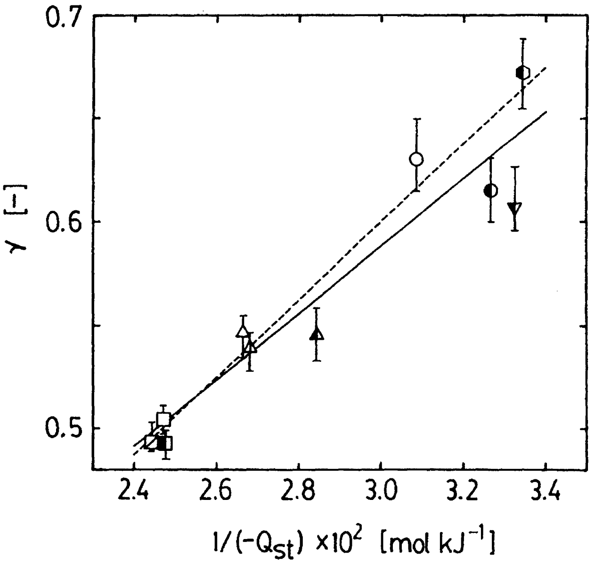

Fig. 4. Correlation between γ and $1/(-Q_{st})$. Symbols: refer to Fig. 1 and Table 2.

Consideration for Linear Correlation between γ and $1/(-Q_{st})$. Figure 5 represents $\ln K_0$ as a linear function of Q_{st}, indicating that an enthalpy–entropy compensation is observed in the adsorption equilibrium in the gaseous system. Similarly, the establishment of an enthalpy–entropy compensation effect has been reported for a retention behavior in reversed-phase liquid chromatography.[14—16] In a previous paper,[12] the authors reported that an enthalpy–entropy compensation occurred in the surface diffusion in gaseous adsorption using ODS-silica-gel as an adsorbent. The linear correlation in Fig. 5 is represented by the following empirical equation:

$$\ln K_0 = a(-Q_{st}) + b = -0.14(-Q_{st}) - 2.4. \qquad (8)$$

According to Eq. 8, both values of K_0 and Q_{st} can be calculated from one datum of K measured at a given temperature.

Figure 6 shows the correlation between D_s and K. The values of D_s and K were determined under intermediate temperature conditions. The experimental data scattered around a solid line. The plots in Fig. 6 probably indicate the establishment of a linear free-energy relation, though the coefficient of the linear correlation is about 0.6. Similar linear correlation have been confirmed in various RP-LC systems.

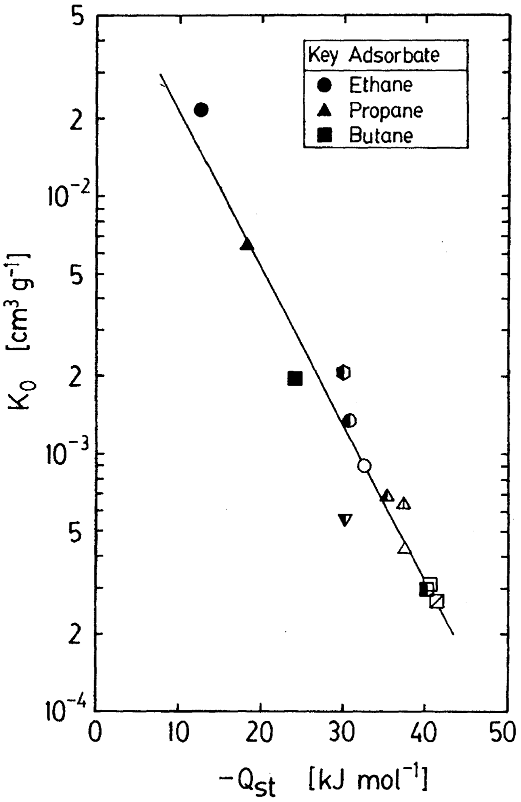

Fig. 5. Correlation between K_0 and Q_{st}. Symbols: refer to Fig. 1 and Table 2.

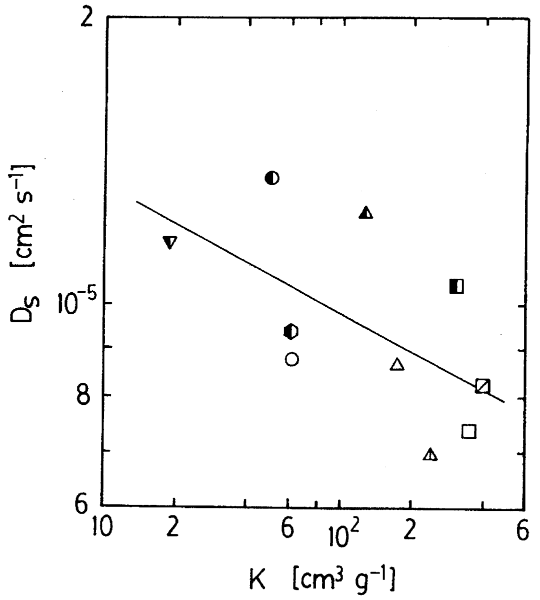

Fig. 6. Correlation between D_s and K. Symbols: refer to Fig. 1 and Table 2.

The following empirical correlation was observed between D_s and K:

$$\ln D_s = A(\ln K) + B = -0.13(\ln K) - 10.9. \qquad (9)$$

The following equation is derived by combining Eqs. 6, 7, 8, and 9:

$$\gamma = -aAR_gT - A - (Ab + B - \ln D_k)R_gT/(-Q_{st}). \qquad (10)$$

According to Eq. 10, γ can be estimated by applying Eqs. 8 and 9. The linear correlation represented by the broken line in Fig. 4 was calculated from the estimated values of γ. Both the solid and broken lines almost agree with each other. It is concluded that γ can be estimated from Q_{st} when the LFER and the enthalpy–entropy compensation in adsorption equilibrium are established.

Estimation of D_s: If Q_{st} is known, D_s can be calculated by Eq. 6, because γ can also be estimated from Q_{st}. The value of D_k can be calculated by Eq. 5. The subject of the prediction of D_s is substituted for that of the estimation of Q_{st}. As mentioned above, Q_{st} can be estimated from one datum of K at a given temperature. Of course, Q_{st} is determined more accurately by the van't Hoff plot of K measured at different temperatures. In conclusion, D_s can be calculated from only one datum of K. Based on the results in Figs. 4 and 5, D_s at different temperatures was calculated from K. Figure 7 shows the comparison of D_s estimated and experimental data. It is indicated that D_s can be estimated from K with an error less than about 50%. The mean-square deviation for all the plots was calculated to be almost 0.23. As indicated in Fig. 6, D_s can be directly approximated from K by an empirical correlation, i.e., Eq. 9. However, D_s at a different temperature cannot be estimated by the correlation. Many correlations representing a linear free-energy relation must be determined for each temperature condition. On the contrary, D_s of various substances at given temperatures can be estimated from only one datum of K measured at a different temperature by combining Eq. 6 and the linear correlation between γ and $1/(-Q_{st})$ illustrated in Fig. 4. As described above, two methods have been already proposed for estimating D_s. Sladek et al. correlated D_s with Q_{st}. However, their method may be applicable only for estimating the order of D_s. Tamon et al. proposed an empirical equation including three constants calculated from the experimental data. They reported that the mean-square deviation for all experimental data was 0.55. However, there are many experimental data which cannot be estimated with errors of less than 50%. The estimation procedure of D_s proposed in this study is superior to the two methods.

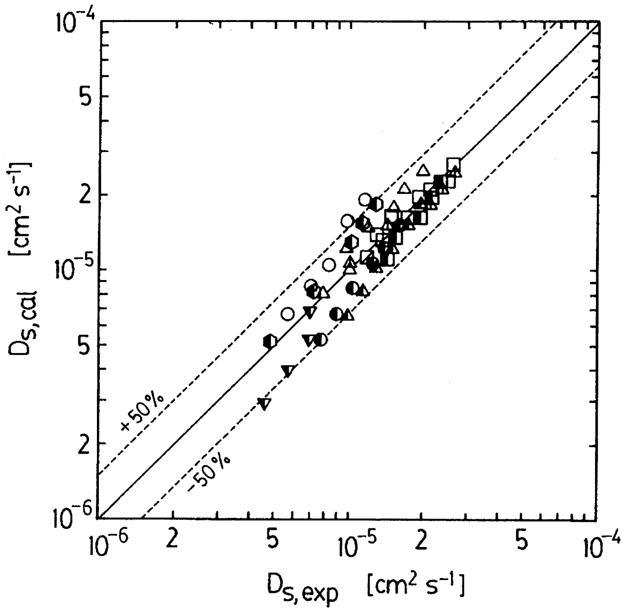

Fig. 7. Comparison of D_s estimated with experimental data. Symbols: refer to Fig. 1 and Table 2.

The values of Q_{st} are plotted against ΔH_v in Fig. 8. As described above, the ratio of $(-Q_{st})/\Delta H_v$ is usually found

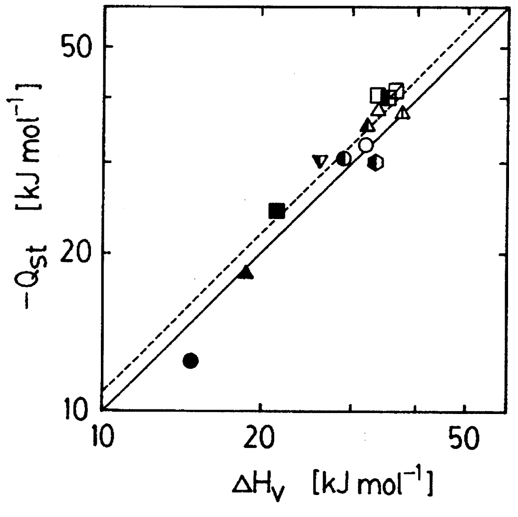

Fig. 8. Correlation between Q_{st} and ΔH_v. Symbols: refer to Fig. 1 and Table 2, and to Fig. 5.

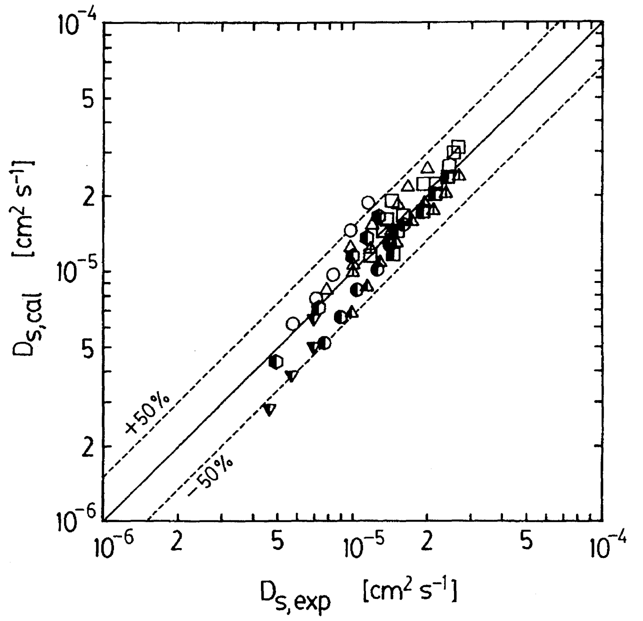

Fig. 9. Comparison of D_s estimated with experimental data. Symbols: refer to Fig. 1 and Table 2.

to range from 1.2 to 1.6 in the case of gas-phase adsorption on a surface. The broken line in Fig. 8 indicates that the average ratio of $(-Q_{st})/\Delta H_v$ is about 1.1 in a gaseous system using the ODS-silica-gel. Similar correlations between Q_{st} and ΔH_v have already been confirmed in a number of gas-phase systems. The ratio $(-Q_{st})/\Delta H_v$ is generally reported to range from about 1.0 to 1.5 for gaseous adsorption on a surface. The presence of correlations between Q_{st} and ΔH_v is not specific for the system in this study. The result in Fig. 8 is consistent with previous observations for the ratio $(-Q_{st})/\Delta H_v$.[2)] An approximate value of D_s can be estimated from ΔH_v, because Q_{st} can be roughly calculated from ΔH_v, by taking the average value of $(-Q_{st})/\Delta H_v$. In Fig. 9, D_s estimated in this manner is compared with the corresponding experimental data. The profile of the plots in Fig. 9 is similar to that in Fig. 7. The results in Fig. 9 indicate that D_s can also be estimated from ΔH_v with an error of less than about 50% with no experimental datum. The mean-square deviation for all of the plots was calculated to be about 0.48. An estimation of D_s is difficult because the D_s value vary extremely with the combination of adsorbates and adsorbents. It is probably possible to accurately an estimate only the order of D_s at present. Under such conditions, the development of an estimation procedure of D_s using no experimental data seems to be meaningful.

Conclusion

An estimation procedure of D_s in gaseous adsorption using the ODS-silica-gel was proposed based on the restricted Knudsen diffusion model, in which D_s was correlated with D_k by introducing E_r. It was indicated that γ of different adsorbates could be correlated with the same linear line between γ and $1/(-Q_{st})$. A linear correlation could be expected when LFER held and enthalpy–entropy compensation in the adsorption equilibrium was established. The value of D_s of various adsorbates at given temperatures in the gaseous system could be calculated from only one datum of K with an error of less than about 50%. Similarly, D_s could be empirically estimated from ΔH_v of the adsorbates without experimental data. The proposed estimation procedure of D_s probably has general applicability, because the effectiveness of the procedure was confirmed in some other gaseous systems,[17)] and because a similar method for estimating D_s was also demonstrated in liquid-phase adsorption systems.[18,19)] However, it is required that the validity of the proposed procedure must be proved in many gas-phase adsorption systems.

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