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Mass-Transfer Phenomena on the Surface of Adsorbents in Reversed-Phase Chromatography

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Characteristics of mass-transfer phenomena on the surface of adsorbents in reversed-phase chromatography were studied by the chromatographic method and moment analysis. Enthalpy-entropy compensation occurs for surface diffusion in various systems of reversed-phase chromatography. The mechanism of surface diffusion seems to be essentially identical regardless of adsorption conditions. The linear free-energy relation holds in reversed-phase liquid chromatographic systems. Analyzing the slope of the linear relations, it is concluded that the activation energy of surface diffusion is essentially smaller than the isosteric heat of adsorption in liquid-phase adsorption as well as in gaseous systems though the heat of adsorption is experimentally determined to be smaller than the activation energy. Surface diffusion coefficients were correlated to physical properties of adsorbates. Concentration dependence of surface diffusion coefficient was explained by the chemical potential driving force model. An estimation method of the surface diffusion coefficient at each given temperature and amount adsorbed in reversed-phase liquid chromatography was proposed.

Introduction

Many kinds of liquid chromatographic techniques are frequently employed for both analytical and preparative separations. Reversed-phase mode is the most widely used among them. It is estimated that about 70–80% of analytical separations have been carried out by using reversed-phase techniques. In the field of reversed-phase liquid chromatography, (octadecylsilyl)silica gel (ODS) is used as a stationary phase in most cases (Krstulovic and Brown, 1982; Poole and Poole, 1991; Sander and Wise, 1987). Quite a few works have been reported on retention behaviors on the surface of ODS. Effects of several parameters such as solvent composition of mobile phase, chain length of chemically bonded ligand, and properties of adsorbate on retention behaviors have been extensively studied.

With extensive utilization of reversed-phase mode, chromatographic separations under complex conditions have been required in order to achieve objective separations. For analytical purposes, the gradient elution method has been frequently used to make fine separations (Jandera and Churacek, 1985). In the case of preparative purifications, chromatographic separations have been usually carried out under overload conditions by using various operation systems such as a simulated moving bed (Hashimoto et al., 1983) and continuous annular chromatography (Howard et al., 1988). Application of simulation strategies must be efficient for optimization of such complex chromatographic systems.

Some simulation models have been proposed (Cretier and Rocca, 1987; Eble et al., 1987a,b; Golshan-Shirazi et al., 1988; Golshan-Shirazi and Guiochon, 1988a,b; Guiochon et al., 1989; Jacobson et al., 1990; Katti and Guiochon, 1990). Applications of the models were attempted as an optimization strategy of chromatographic separations. The models, however, may not be extensively employed for various chromatographic techniques such as gradient elution method, displacement chromatography, and heavily

overloaded separations, because mass-transfer rates in a column were represented by using an overall kinetic parameter. The contributions of several mass-transfer resistances in a column to chromatographic efficiency cannot be considered separately. Effects of various chromatographic conditions, for example, mobile-phase compositions and amounts of sample substance adsorbed, on mass-transfer rate cannot be taken into account quantitatively.

In order to simulate chromatographic separation processes in a column and to make a rational design of chromatographic systems for separation of mixtures, information on adsorption rate as well as adsorption equilibrium of each component is essential. All mass-transfer steps in a column have contributions to peak broadening and column efficiency in chromatographic separations. Axial dispersion and fluid-to-particle mass-transfer phenomena have been studied in detail in the field of chemical engineering. It has also been made possible to estimate pore diffusivity or Knudsen diffusivity in adsorbent particles.

A great number of studies have been carried out on adsorption equilibria (retention behaviors) in reversed-phase liquid chromatography (Berendsen and de Galan, 1980; Hennion et al., 1978; Horvath et al., 1976, 1977, 1978; Karch et al., 1976a,b; Karger et al., 1976; Lochmuller and Wilder, 1979; Majors and Hopper, 1974; Schoenmakers et al., 1979). Very few works, however, have been carried out so far on diffusion phenomena in reversed-phase packing materials, in contrast to extensive studies concerning retention behaviors. Detailed analyses of adsorption and mass-transfer phenomena on the surface of packing materials must be essential to construct an accurate simulation model of chromatographic separations. In previous papers (Miyabe and Suzuki, 1992, 1993a,b, 1994a,c), it was clarified that intraparticle diffusion contributed to overall mass-transfer resistance, and that surface diffusion had an extremely important role for the migration of adsorbed molecules in ODS particles. The surface diffusion coefficient increased with an increase in

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the amount adsorbed. The positive concentration dependence of surface diffusion coefficient could be interpreted in terms of diffusion by a chemical potential driving force. Kinetic studies on surface diffusion phenomena on reversed-phase packing materials must provide significant information about the separation mechanism of reversed-phase chromatography. Accurate estimation of surface diffusion coefficient must be required in order to predict chromatographic profiles. Though several methods have been proposed for the purpose, many subjects still remain for estimation of the surface diffusion coefficient.

Gilliland et al. (1974) proposed an estimation method of surface diffusion coefficients in gaseous systems. Surface diffusion coefficients were calculated from corresponding isosteric heats of adsorption. According to this idea Sladek et al. (1974) rearranged many experimental data in a wide range from physisorption to chemisorption and proposed an empirical correlation to estimate surface diffusion coefficients in gas-phase adsorption. Mitani et al. (1972) studied the relationship between the Henry constant and the surface diffusion coefficient and reported that the ratio of activation energy of surface diffusion to isosteric heat of adsorption ranged from 0.3 to 1.0. For liquid-phase adsorption, Suzuki and Kawazoe (1975) studied liquid-phase adsorption of volatile organics from aqueous solution to an activated carbon and determined surface diffusion coefficients by using the batch adsorption technique. A linear relation was confirmed between surface diffusion coefficients and the ratio of the boiling point of the adsorbates to adsorption temperature. The surface diffusion coefficient in the activated carbon can be estimated from the linear relationship. They suggested that the ratio of activation energy of surface diffusion to isosteric heat of adsorption was about 0.5 by analyzing the slope of the linear plot, and provided physical interpretation to the frequency factor on the basis of the hopping model.

In previous papers (Miyabe and Suzuki, 1992, 1993a,b, 1994a-c), the authors studied adsorption characteristics of reversed-phase chromatography, in which ODS and methanol/water mixture were mainly used. It was confirmed that isosteric heats of adsorption in liquid-phase adsorption were apparently found to be smaller than corresponding values in gaseous systems, and that this result was attributed to the influence of solvent on liquid-phase-adsorption phenomena. In reversed-phase liquid chromatography, various kinds of organic solvents are used and the gradient elution method is also employed, in which mobile-phase composition is gradually changed according to the progress of chromatographic separation. Because the isosteric heat of adsorption, activation energy of surface diffusion, and surface diffusion coefficient in liquid-phase adsorption are varied with a change in mobile-phase composition, the surface diffusion coefficient cannot be estimated from the isosteric heat of adsorption.

Because surface diffusion coefficients significantly vary with the combination of adsorbents and adsorbates, the estimation methods previously proposed may not be applied to a given experimental system. Extensive studies on surface diffusion phenomena have been made in order to analyze the migration mechanism on a surface, and to develop an estimation method of surface diffusion coefficients. No work, however, has been carried out so far on surface diffusion phenomena in reversed-phase liquid chromatography.

This paper is concerned with surface diffusion phenomena in reversed-phase liquid chromatography. Pulse response experiments were made under various chro-

matographic conditions. In liquid-phase adsorption, four kinds of reversed-phase packing materials having different *n*-alkyl chains were used as a stationary phase. Methanol/water mixed solvents of various compositions, namely 40–100 vol % methanol were used as a mobile phase. Several organic compounds were employed as an adsorbate. Comparing with liquid-phase adsorption, chromatographic measurements were carried out in gaseous systems, in which adsorption characteristics were not influenced by the presence of a solvent. In gas-phase adsorption, ODS were used as a stationary phase and helium as a carrier gas. On the basis of experimental results an estimation method of surface diffusion coefficients was proposed.

Moment Analysis

Chromatographic peaks leaving from a column were analyzed by the method of moments (Suzuki, 1973, 1990). The adsorption equilibrium constant was determined from first moment analysis. Second moment analysis provided information about all the mass-transfer steps involved in adsorption processes. The intraparticle diffusion coefficient was determined by subtracting the effects of axial dispersion and fluid-to-particle mass transfer.

The first absolute moment and the second central moment of a chromatographic peak are expressed as follows:

$$\mu_1 = \int C_e(t)t \, dt / \int C_e(t) \, dt = (z/u_0)\delta_0 \quad (1)$$

$$\mu_2' = \int C_e(t)(t - \mu_1)^2 \, dt / \int C_e(t) \, dt = (2z/u_0)(\delta_{ax} + \delta_f + \delta_d) \quad (2)$$

where

$$\delta_0 = \epsilon + (1 - \epsilon)(\epsilon_p + \rho_p K) \quad (3)$$

$$\delta_{ax} = (Ez/u_0^2)\delta_0^2 \quad (4)$$

$$\delta_f = (1 - \epsilon)(R/3k_f)(\epsilon_p + \rho_p K)^2 \quad (5)$$

$$\delta_d = (1 - \epsilon)(R^2/15De)(\epsilon_p + \rho_p K)^2 \quad (6)$$

The first moment was analyzed by eq 7 derived from eq 1 in the following way.

$$(\mu_1 - t_0)/(1 - \epsilon) = (z/u_0)\rho_p K \quad (7)$$

where

$$t_0 = (z/u_0)[\epsilon + (1 - \epsilon)\epsilon_p] \quad (8)$$

According to eq 7, a linear relationship should be observed between $(\mu_1 - t_0)/(1 - \epsilon)$ and (z/u_0) . The adsorption equilibrium constant, K , was calculated from the slope of the plot.

For analysis of the second moment, a parameter H was calculated as follows:

$$H = (\mu_2'/\mu_1^2)(z/2u_0) = (Ez/u_0^2) + H_0 \quad (9)$$

$$H_0 = \delta_d/\delta_0^2 \quad (10)$$

The value of δ_f was calculated from eq 5, and its contribution to second moment was corrected. The fluid-to-particle mass-transfer coefficient, k_f , was estimated by

the equation of Wilson-Geankoplis for liquid-phase adsorption.

$$Sh = (1.09/\epsilon)Sc^{1/3}Re_p^{1/3} \quad (11)$$

For gaseous systems, the value of k_f was calculated by the equation of Carberry.

$$Sh = (1.15/\epsilon^{1/2})Sc^{1/3}Re_p^{1/2} \quad (12)$$

Molecular diffusivity, D_m , of an adsorbate in methanol-water mixture was estimated by the Wilke-Chang equation.

$$D_m = 7.4 \times 10^{-8} (a_2 M_2)^{1/2} T / \eta_2 V_1^{0.6} \quad (13)$$

For gaseous systems, the value of D_m was estimated by the Hirschfelder equation.

$$D_m = 0.1883 [T^3 (M_i + M_j) / M_i M_j]^{1/2} / P \sigma_{ij}^2 \Omega_D \quad (14)$$

The contribution of adsorption rate at an adsorption site to the second moment was assumed to be negligibly small. The plot of H vs $1/u_0$ provides the axial dispersion coefficient, E_z , and the intraparticle diffusivity, D_e , from a slope and an intercept, respectively. Intraparticle diffusivity is related to both pore diffusivity, D_p , and surface diffusion coefficient, D_s , as follows:

$$D_e = D_p + \rho_p K(D_s) \quad (15)$$

Pore diffusivity was estimated from the molecular diffusivity, porosity, and tortuosity factor of pores by the following equation for liquid-phase adsorption.

$$D_p = (\epsilon_p/k^2)D_m \quad (16)$$

The tortuosity factor was determined from chromatographic experiments with inert pulses. In gaseous adsorption systems, Knudsen diffusion was dominant compared with molecular diffusion in this study. Pore diffusivity was calculated from Knudsen diffusivity instead of molecular diffusivity according to eq 16. Knudsen diffusivity was calculated by the following equation.

$$D_K = (2/3)R_p(8R_g T/\pi M)^{1/2} \quad (17)$$

When an elution peak can be approximated by the normal distribution curve, first and second moments can be determined from the position and the width of a peak, respectively. The experimental first moment $\mu_{1\text{exp}}$ includes the effects of the volume, V_e , of the pipes between an injection port and a column and that between a column and a detector. The correction of the extracolumn volume was made for $\mu_{1\text{exp}}$ as follows:

$$\mu_1 = \mu_{1\text{exp}} - V_e/v \quad (18)$$

The second moment was calculated from a peak width at half-height, w , by the following equation.

$$\mu_2' = w^2/5.54 \quad (19)$$

The contribution of the extracolumn pipes to the second moment was measured by the chromatographic method without a column, and it was corrected. The effects of the first and the second moments of a pulse introduced at the inlet of a column were neglected because pulse size was extremely small. As described above, in this study some

corrections were made in order to estimate surface diffusion coefficients from second moments experimentally observed. The influence of these corrections on the accuracy of surface diffusion coefficients estimated is discussed in the Appendix.

Experimental Section

Apparatus. A high-performance liquid chromatograph was employed for liquid-phase adsorption. A small volume of sample solutions was introduced into a fluid flow by use of a sample injector. A thermostated water bath was employed to maintain column temperature at a constant level. The concentration of the sample in effluent was monitored by a ultraviolet or refractive index detector.

Pulse response measurements in gaseous systems were carried out by using a conventional gas chromatograph equipped with a thermal conductivity detector (TCD). The flow rate of a carrier gas was determined by a soap film flowmeter at the outlet of the detector. A pulse of an adsorbate gas was introduced into the carrier gas flow by use of a gastight syringe. The concentration of an adsorbate in effluent was monitored by the detector. A column was kept at a constant temperature in a thermostated methanol-water mixture bath or in a column oven of the gas chromatograph.

Columns and Reagents. Properties of the columns (YMC) used in liquid-phase adsorption are shown in Table 1. The size of the columns was 6 mm in inside diameter and 150 mm in length. Four kinds of monofunctional reversed-phase packing materials having different alkyl chains were employed. 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). The average particle diameter was about 45 μm . The mobile phase was mixture of methanol and pure water, in which the volumetric composition of methanol was changed in the range from 40 to 100 (vol %). As a sample material, several organic compounds such as *n*-alkanes, *n*-alcohols, benzene derivatives, *p*-*n*-alkylphenols, and aromatic hydrocarbons were used, and as an inert substance, uracil was employed.

In gaseous adsorption systems, an ODS packed column was employed. Properties of the column are also listed in Table 1. The average diameter of the spherical ODS was determined to be 296 μm by a scanning electron microscope. Pore-related properties were determined by the nitrogen adsorption method. The ODS was synthesized with a monofunctional, *n*-octadecyldimethylsilyl, ligand. Carbon content was 19.8 wt %. This figure is close to the maximum amount of carbon, which can be introduced on the surface of silica gel by chemical bonding of *n*-octadecyldimethylsilyl ligand. The size of the column was 3.2 mm in inside diameter and 195 mm in length. The properties of the column were estimated from column volume, mass of the adsorbent, and particle apparent density. Helium was used as a carrier gas. The purity of the carrier gas was 99.9%. Several organic compounds such as *n*-alkanes and benzene derivatives, whose boiling point was lower than about 410 K, were employed as an adsorbate.

Procedure. Experimental conditions in liquid-phase adsorption are shown in Table 1. Pulse response experiments were made at zero and various surface coverages with varying temperature and flow rate of a mobile phase. Small concentration perturbation pulses were introduced into a fluid flow. Measurements of chromatographic peaks were made in the temperature range from 288 to 308 K. The volumetric flow rate of a mobile phase was varied in

Table 1. Properties of Columns and Experimental Conditions

	liquid phase				gas phase
column	TMS	C4	C8	ODS	ODS
av particle diam, d_p (μm)	45	45	45	45	296
particle density, ρ_p (g/cm^3)	0.74	0.73	0.75	0.86	0.95
true density (g/cm^3)	1.94	1.85	1.65	1.60	1.51
porosity, ϵ_p	0.62	0.61	0.55	0.46	0.37
carbon content (wt %)	4.1	6.7	9.9	17.1	19.8
ligand density (nm^{-2})	2.7	2.2	2.0	1.9	
mass of adsorbent (g)	1.9	1.8	1.8	2.1	1.03
column size (mm)		6×150			3.2×195
void fraction, ϵ	0.44	0.42	0.42	0.43	0.31
Peclet number, Pe	0.65	0.93	0.62	1.02	
tortuosity factor, k^2	4.1	4.6	4.4	4.5	8.4
column temp (K)		288–308			260–418
mobile phase (carrier gas)		methanol/water: 100/0–40/60 (vol %)			helium
superficial velocity, u_0 (cm/s)		0.06–0.12			7.1–14.1
sample material		benzene derivatives, phenol derivatives, <i>n</i> -alcohols, <i>n</i> -alkanes, polyaromatic hydrocarbons			

the range from 0.017 to 0.033 cm^3/s . This corresponded to the range of superficial velocity from 0.059 to 0.118 cm/s .

Measurements of chromatographic peaks were similarly carried out in gaseous adsorption systems at zero surface coverage. The column temperature was changed in the range from 260 to 418 K. The volumetric flow rate of the carrier gas was changed in the range from 0.5 to 1.0 cm^3/s . This corresponded to the range of superficial velocity from 7.1 to 14.1 cm/s . A small pulse of an adsorbate gas was injected into a carrier gas flow at the inlet of a column. Chromatographic peaks measured in both gas- and liquid-phase-adsorption systems were analyzed by the method of moments (Suzuki, 1973, 1990).

Results and Discussion

Correlation of Surface Diffusion Coefficient with Properties of Adsorbates. As a first approximation, it was assumed that surface migration could be regarded as a tracer diffusion of an adsorbate molecule in *n*-octadecane. An empirical equation was proposed for the prediction of a tracer diffusivity in binary systems involving long-chain hydrocarbons (Chen and Chen, 1985).

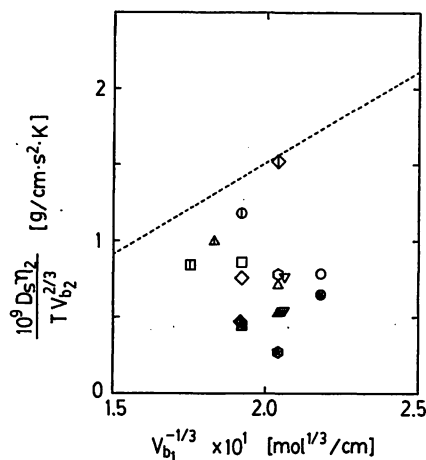
$$10^9 D_{12} \eta_2 / TV_{b2}^{2/3} = 11.96 V_{b1}^{-1/3} - 0.8796 \quad (20)$$

Figure 1 shows comparison of experimental data with the value of the left-hand side of eq 20. Sufficient agreement could not be observed between experimental and calculated results. Especially in liquid-phase adsorption, experimental data were about 1 order of magnitude smaller than calculated values. The difference between the experimental and calculated results may be attributed to several factors. For example, the influence of the tortuosity factor of the surface of ODS particles on surface diffusion should be considered. The mobility of *n*-octadecylsilyl ligands seems to be restricted in comparison with the liquidlike state of *n*-octadecane because one end of the alkyl chain is chemically bonded on the surface of silica gel. The properties of the bonded ligands may be influenced by solvation with a mobile phase.

In Figure 2 surface diffusion coefficients experimentally determined were plotted against $V_b^{-1/3}$ in the same manner in eq 20. A linear relationship was observed, and it was expressed by the following equation.

$$D_s = 1.1 \times 10^{-8} \exp(26.1 V_b^{-1/3}) \quad (21)$$

In Figure 3 surface diffusion coefficients were plotted against the ratio of the boiling point of adsorbates to



Key	Adsorbate	
◇	<i>n</i> -Pentane	Gas Phase Adsorption
○	<i>n</i> -Hexane	
△	<i>n</i> -Heptane	
□	<i>n</i> -Octane	
○	Benzene	
△	Toluene	
□	Ethylbenzene	
◇	<i>p</i> -Xylene	
▽	Chlorobenzene	
○	cyclo-Hexane	
●	Benzene	Liquid Phase Adsorption
▲	Toluene	
■	Ethylbenzene	
◆	<i>p</i> -Xylene	
●	cyclo-Hexane	

Figure 1. Comparison of surface diffusion coefficients calculated by eq 20 with experimental data for both gas- and liquid-phase-adsorption systems.

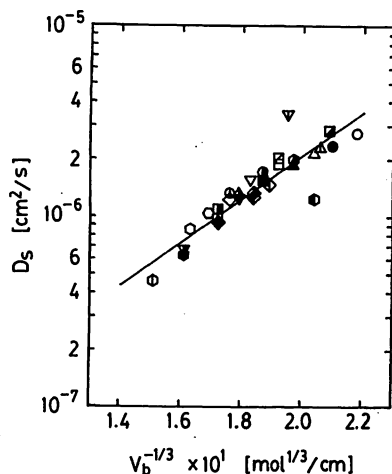
adsorption temperature (Suzuki et al., 1975). The value of the boiling point of a polar substance was estimated from that of a corresponding nonpolar homologue, because only the hydrophobic part of adsorbate molecules should contribute adsorption phenomena on ODS. Experimental data scattered around straight lines representing the following empirical correlations.

$$D_s = 4.3 \times 10^{-5} \exp(-2.3 T_b / T) \quad n\text{-alkylbenzenes} \quad (22)$$

$$D_s = 5.4 \times 10^{-5} \exp(-2.6 T_b / T) \quad n\text{-alkylphenols} \quad (23)$$

$$D_s = 4.1 \times 10^{-5} \exp(-2.7 T_b / T) \quad n\text{-alcohols} \quad (24)$$

Because the value of the boiling point and molar volume



Key	Adsorbate	Key	Adsorbate	Key	Adsorbate
○	Benzene	●	n-Hexanol	⊕	Binaphthyl
△	Toluene	▲	n-Heptanol	⊞	Anthracene
□	Ethylbenzene	▼	n-Octanol	▽	Nitrobenzene
◇	n-Propylbenzene	■	n-Decanol	△	Chlorobenzene
◇	n-Butylbenzene	▼	n-Pentane	△	Aniline
◇	n-Amylbenzene	●	n-Hexane	⊞	Acetophenone
○	n-Hexylbenzene	▲	n-Heptane	⊞	Methylacetophenone
⊞	p-Xylene	■	n-Octane	◇	Ethylacetophenone
●	Phenol	⊕	cyclo-Hexanol	⊞	Methylbenzoate
▲	p-Cresol	●	cyclo-Hexane	⊞	Ethylbenzoate
■	p-Ethylphenol	⊕	Biphenyl	◇	n-Propylbenzoate
▼	p-n-Propylphenol	◇	Naphthalene		
◆	p-n-Butylphenol	◇	1-Naphthol		
●	p-n-Hexylphenol	◇	2-Naphthol		

Figure 2. Plot of surface diffusion coefficient against $V_b^{-1/3}$. V_b : molecular volume at boiling point (cm^3/mol).

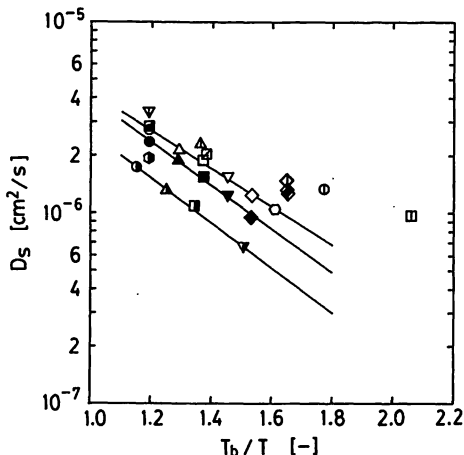


Figure 3. Plot of surface diffusion coefficient against T_b/T . T_b : boiling point of adsorbate (K). T : adsorption temperature (K). Symbols: refer to Figure 2.

of an adsorbate at normal boiling point can be determined from experiment or calculation methods, eqs 21–24 are available in practice to estimate surface diffusion coefficients on ODS particles.

As shown in previous papers (Awum et al., 1988; Ching et al., 1989; Ma et al., 1988; Miyabe and Suzuki, 1992, 1993a, 1994b), the isosteric heat of adsorption, Q_{st} , experimentally measured is smaller than activation energy of surface diffusion, E_s , in liquid-phase adsorption. In contrast, in gaseous systems the ratio of E_s/Q_{st} was found to be about 0.5 for surface diffusion (Gilliland et al., 1974; Sladek et al., 1974; Chihara et al., 1978). The difference of thermodynamic properties of adsorption processes in both liquid- and gas-phase systems may result from the solvent effect. In a previous paper (Miyabe and Suzuki, 1994b), the authors analyzed quantitatively the influence of a solvent on adsorption equilibrium and the isosteric

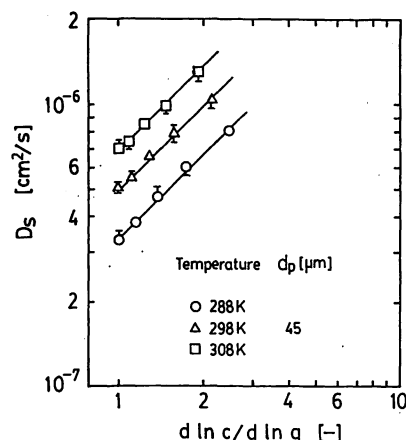


Figure 4. Plot of D_s vs $(d \ln c / d \ln q)$.

heat of adsorption on the basis of the solvophobic theory. It was confirmed that Q_{st} was measured to be an apparently small value as compared with a corresponding value in gas-phase adsorption. With consideration of Trouton's rule, the slope of the linear plot in Figure 3 may suggest the approximate value of the ratio of E_s/Q_{st} . In this study the ratio of E_s/Q_{st} was ranging from about 0.2 to 0.3. These values were consistent with the value of E_s/Q_{st} experimentally determined in gas-phase-adsorption systems with ODS (Miyabe and Suzuki, 1993a,b). By analyzing surface diffusion coefficients, it was also concluded that the activation energy of surface diffusion was smaller than the isosteric heat of adsorption in the liquid-phase-adsorption system.

Concentration Dependence of Surface Diffusion Coefficient. Concentration dependence of diffusivity in porous materials on the amount adsorbed has been reported in both gas- and liquid-phase-adsorption systems (Ruthven and Loughlin, 1971; Gilliland et al., 1974; Kawazoe et al., 1974; Okazaki et al., 1981; Takeuchi et al., 1984; Costa et al., 1985). In liquid-phase adsorption the concentration dependence of the surface diffusion coefficient has been explained by the change in adsorption energy (Komiya and Smith, 1974; Neretnieks, 1976; Sudo et al., 1978; Suzuki and Fujii, 1982; Moon and Lee, 1983; Muraki, 1982). As reported in previous papers (Miyabe and Suzuki, 1992, 1993a), adsorption characteristics of *p*-tert-octylphenol (PTOP) on ODS were studied by using methanol/water mixed solvent (70/30 vol %) as a mobile phase. The surface diffusion coefficient increased with an increase in the amount of PTOF adsorbed in the reversed-phase liquid chromatographic system. Both isosteric heat of adsorption and activation energy of surface diffusion, however, were almost constant irrespective of the amount adsorbed. As shown in Figure 4, the positive concentration dependence of the surface diffusion coefficient of PTOF could be interpreted in terms of diffusion by the chemical potential driving force according to the following equation.

$$D_s(q) = D_s(0)(d \ln c / d \ln q) \quad (25)$$

The value of $(d \ln c / d \ln q)$ was calculated from adsorption isotherms of PTOF measured separately. This result suggests that the surface diffusion coefficient at each given amount adsorbed can be estimated from an adsorption isotherm and a surface diffusion coefficient at a certain amount adsorbed.

Enthalpy-Entropy Compensation Effect in Surface Diffusion Phenomena. Temperature dependence

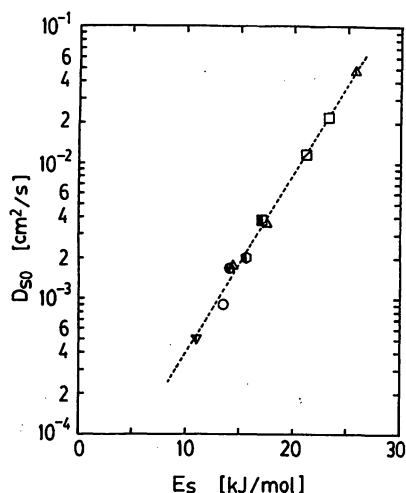


Figure 5. Correlation of frequency factor with activation energy of surface diffusion for gas-phase adsorption on ODS. Symbols: refer to Figure 2.

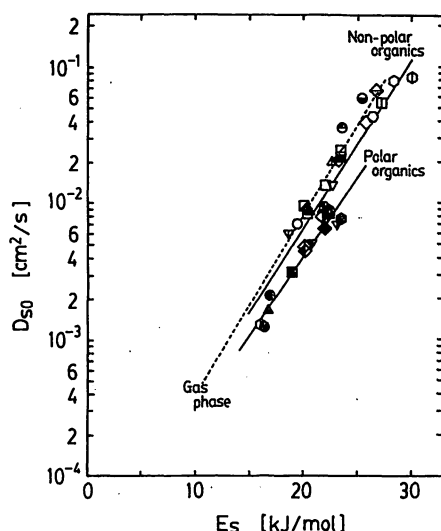


Figure 6. Correlation of frequency factor with activation energy of surface diffusion for liquid-phase adsorption on ODS. Symbols: refer to Figure 2.

of surface diffusion coefficient was analyzed according to the Arrhenius equation.

$$d \ln D_s / d(1/T) = -E_s / R_g \quad (26)$$

Activation energy of surface diffusion, E_s , and frequency factor, D_{s0} , was calculated from the slope and the intercept of the Arrhenius' plot. The correlation of E_s and D_{s0} is shown in Figure 5 for gas-phase adsorption, in which ODS was used as a stationary phase and helium was used as a carrier gas. A linear relation was observed, on which experimental data for nonpolar organics such as saturated hydrocarbons and benzene derivatives could be plotted. It is concluded that the enthalpy-entropy compensation effect can be observed for surface diffusion phenomena in gaseous systems.

Similar plots are shown in Figure 6 for various kinds of adsorbates in liquid-phase adsorption, in which ODS was used as a stationary phase and methanol/water mixture (70/30 vol %) was used as a mobile phase. The dotted line in Figure 6 represents the correlation for gas-phase-adsorption systems in Figure 5. A similar correlation could be observed for nonpolar adsorbates. On the other hand, a separate linear relationship having almost the same slope was obtained for polar substances such as *n*-alcohols and phenol derivatives.

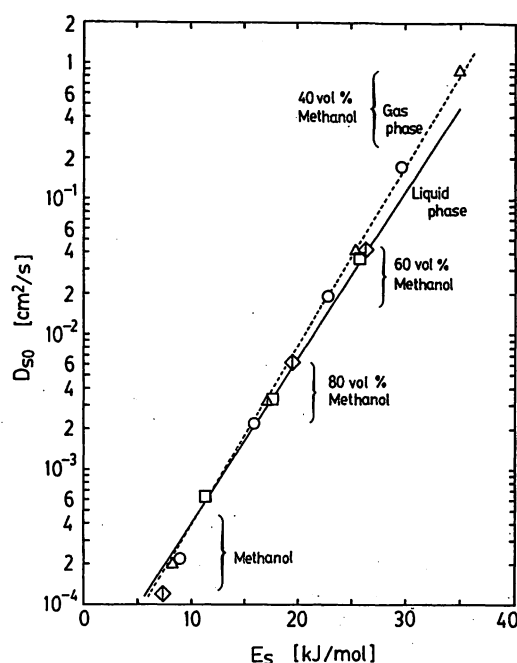


Figure 7. Correlation of frequency factor with activation energy of surface diffusion for liquid-phase adsorption with methanol-water mixtures of various compositions. Symbols: refer to Figure 2.

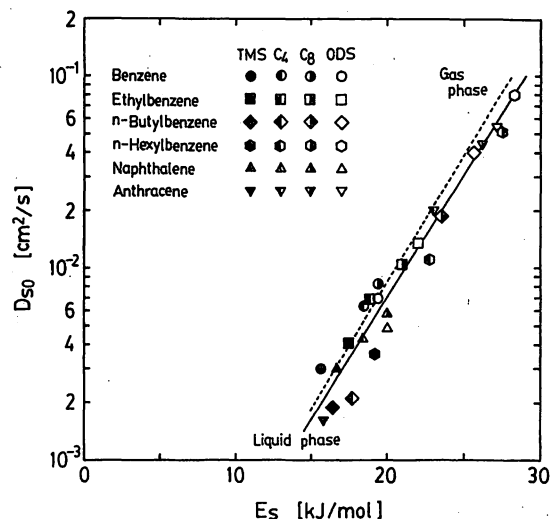


Figure 8. Correlation of frequency factor with activation energy of surface diffusion for liquid-phase adsorption with various stationary bonded phases.

Figure 7 shows the plot of E_s vs D_{s0} for liquid-phase adsorption under the conditions that the stationary phase was ODS and the mobile phase was methanol/water mixed solvents (100/0–40/60 vol %). The dotted and solid lines in Figure 7 represent the correlations for various nonpolar substances in gas- and liquid-phase adsorption, respectively. Experimental data could be plotted on the linear relationship irrespective of methanol composition in a mobile phase.

Experimental data measured by using various kinds of stationary phases are similarly plotted in Figure 8. The carbon number of alkyl chains chemically bonded on the surface of silica gel was changed stepwise from 1 to 18 (TMS–ODS). Nonpolar substances such as benzene derivatives and polyaromatic hydrocarbons were used as the adsorbate and methanol/water mixed solvent (70/30 vol %) and was as the mobile phase. Experimental data scattered around the straight lines described above (dotted and solid lines) regardless of both the kind of adsorbates and the length of the alkyl chains.

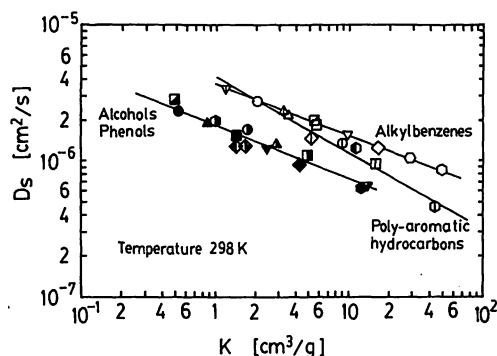


Figure 9. Correlation of surface diffusion coefficient with adsorption equilibrium constant for liquid-phase adsorption on ODS. Symbols: refer to Figure 2.

Enthalpy-entropy compensation effects were already reported for adsorption equilibrium in reversed-phase liquid chromatography. The compensation temperature was found to range from about 500 to 700 K (Knox and Vasvari, 1973; Melander et al., 1979; Woodburn et al., 1989). In this study it was confirmed that enthalpy-entropy compensation occurs for surface diffusion in various systems of adsorbents, carriers, and adsorbates in reversed-phase gas and liquid chromatography, and that the correlation between E_s and D_{s0} could be expressed by straight lines irrespective of adsorption conditions. The mechanism of surface diffusion seems to be essentially identical regardless of composition of an organic solvent in the mobile phase, chemical nature of adsorbate molecules, and alkyl chain length of reversed-phase packing materials. The surface diffusion mechanism in gaseous systems is also likely to be similar to that in liquid-phase adsorption.

The compensation effects observed for surface diffusion can be expressed by the following empirical equations for various adsorbates in reversed-phase gas and liquid chromatographic systems.

$$\ln D_{s0} = 0.305E_s - 10.9$$

nonpolar substances (gas phase) (27)

$$\ln D_{s0} = 0.283E_s - 10.7$$

nonpolar substances (liquid phase) (28)

$$\ln D_{s0} = 0.269E_s - 10.9$$

alcohols, phenols (liquid phase) (29)

By using eqs 27–29, both activation energy and frequency factor of surface diffusion can be calculated from one value of surface diffusion coefficient estimated or experimentally measured. Thus the value of surface diffusion coefficient at each given temperature can be estimated by the Arrhenius equation.

Linear Free-Energy Relation in Reversed-Phase Liquid Chromatography. A linear free-energy relation such as the Hammett rule and the Brensted catalytic rule can be expected to hold when the enthalpy-entropy compensation effects are established. Figure 9 shows the correlation between adsorption equilibrium constants and surface diffusion coefficients for various adsorbates in reversed-phase liquid chromatography. Three different linear relations were observed for *n*-alkylbenzenes, polyaromatic hydrocarbons, and polar substances such as *n*-alcohols and phenols. They are represented by the following equations.

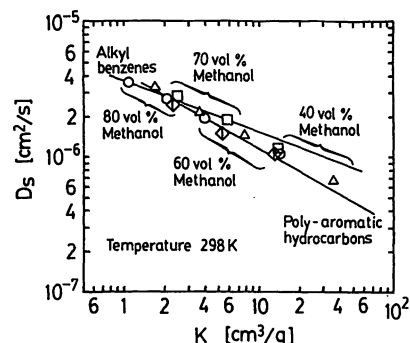


Figure 10. Correlation of surface diffusion coefficient with adsorption equilibrium constant for liquid-phase adsorption with methanol-water mixtures of various compositions. Symbols: refer to Figure 2.

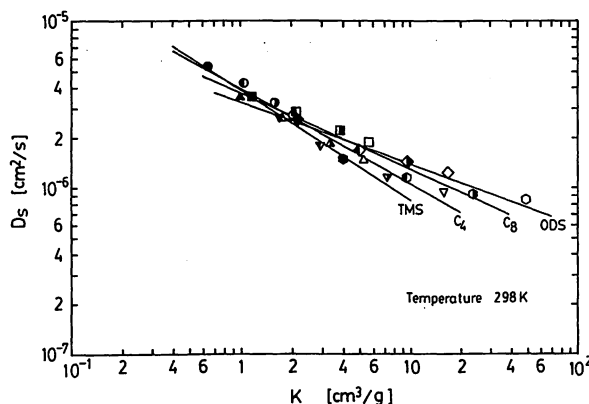


Figure 11. Correlation of surface diffusion coefficient with adsorption equilibrium constant for liquid-phase adsorption with various stationary bonded phases. Symbols: refer to Figure 2.

$$\ln D_s = -0.376 \ln K - 12.5 \quad n\text{-alkylbenzenes} \quad (30)$$

$$\ln D_s = -0.560 \ln K - 12.4 \quad \text{polyaromatic hydrocarbons} \quad (31)$$

$$\ln D_s = -0.394 \ln K - 13.2 \quad \text{alcohols, phenols} \quad (32)$$

Absolute values of the slope are found to be ranging from about 0.3 to 0.6.

Similar plots between K and D_s obtained under the conditions that various methanol/water mixed solvents of different compositions were used as a mobile phase are shown in Figure 10. The two solid lines in the figure are the correlations for *n*-alkylbenzenes and polyaromatic hydrocarbons illustrated in Figure 9. Experimental data could be plotted around the two linear relations regardless of methanol composition in a mobile phase.

As shown in Figure 11, linear relations were also observed between K and D_s when several kinds of adsorbents having various alkyl chains were used as a stationary phase. Though the slope of the straight lines depends on the carbon number of the alkyl chains, absolute values of the slope were smaller than unity.

It is concluded that the linear free-energy relation holds in reversed-phase liquid chromatography irrespective of composition of methanol in a mobile phase, chemical nature of adsorbate molecules, and alkyl chain length of reversed-phase packing materials. The value of the surface diffusion coefficient can be estimated from the adsorption equilibrium constant estimated or experimentally determined. A great number of studies have been carried out for retention behaviors in reversed-phase liquid chromatography (Krstulovic and Brown, 1982; Poole and Poole, 1991; Sander and Wise, 1987). Both empirical and

theoretical methods have also been proposed for estimation of the adsorption equilibrium constant, which are based on several kinds of empirical parameters or the solvophobic theory (Belfort et al., 1984; Mockel et al., 1987; Miyabe and Suzuki, 1994b). These results make it possible to apply conventional studies regarding adsorption equilibrium in reversed-phase liquid chromatography to the estimation of surface diffusion coefficient.

The slope of the linear relations in Figures 9–11 suggests that the ratio of activation energy of surface diffusion to isosteric heat of adsorption ranges from about 0.3 to 0.6, because the figure of the slope is equal to the value of E_s/Q_{st} . This result is consistent with the experimental data in gaseous systems (Miyabe and Suzuki, 1993a,b) and the result obtained by analyzing the relationship between D_s and the ratio of boiling point of adsorbates to experimental temperature (Miyabe and Suzuki, 1994a). Similarly Mitani et al. (1972) studied the correlation between the Henry constant and the surface diffusion coefficient for various gas-phase-adsorption systems, in which several kinds of adsorbents and adsorbates were employed. Linear relations were observed for the systems, and it was reported that the ratio of E_s/Q_{st} ranged from about 0.3 to 1.0. By analyzing the correlation between K and D_s , it was also concluded that the value of E_s was smaller than Q_{st} in liquid-phase adsorption as well as in a gaseous system.

Estimation of Surface Diffusion Coefficient. On the basis of the results described above, the following procedure can be proposed for estimation of the surface diffusion coefficient in a reversed-phase liquid chromatographic system.

1. The surface diffusion coefficient at 298 K is calculated from the molecular volume of an adsorbate at the boiling point by using eq 21 or from the boiling point by eqs 22–24. The value of D_s at 298 K can also be estimated from the adsorption equilibrium constant based on the linear free-energy relations in Figures 9–11.

2. The surface diffusion coefficient at each given temperature can be calculated from D_s experimentally determined or estimated from procedure 1 by considering the enthalpy–entropy compensation effect of surface diffusion phenomena. Similarly the value of D_s at each given amount adsorbed can also be estimated from D_s at 298 K on the basis of the chemical potential driving force model.

According to procedures 1 and 2, the surface diffusion coefficient at each given temperature and amount adsorbed can be estimated from either physical properties of an adsorbate molecule or the adsorption equilibrium constant.

Conclusion

Characteristic of mass-transfer phenomena on the surface of adsorbents in reversed-phase liquid chromatography were studied by the chromatographic method and moment analysis. An estimation method of the surface diffusion coefficient was also proposed based on the experimental results. Pulse response experiments were carried out for various gas- and liquid-phase-adsorption systems, in which the nature and concentration of adsorbates, adsorbents, and carriers were changed. Surface diffusion coefficients were calculated from the second moment of pulse response curves at various temperatures and amounts adsorbed.

Surface diffusion coefficients could be correlated to the properties of adsorbate molecules, namely boiling point or molecular volume at the boiling point. Because the value of the physical properties can be determined from

experiment or calculation methods, eqs 21–24 are available in practice to estimate surface diffusion coefficients on ODS particles.

The positive concentration dependence of the surface diffusion coefficient in a reversed-phase liquid chromatographic system could be interpreted in terms of diffusion by the chemical potential driving force. It is suggested that the surface diffusion coefficient at each given amount adsorbed can be estimated from an adsorption isotherm and a surface diffusion coefficient at a certain amount adsorbed.

The temperature dependence of the surface diffusion coefficient was analyzed according to the Arrhenius equation. Correlations between the activation energy and the frequency factor of surface diffusion were studied under various adsorption conditions. It was confirmed that enthalpy–entropy compensation occurs for surface diffusion in various systems of adsorbents, solvents, and adsorbates in reversed-phase liquid chromatography, and that the correlation between E_s and D_{s0} could be expressed by straight lines irrespective of adsorption conditions. The mechanism of surface diffusion seems to be essentially identical regardless of the composition of methanol in a mobile phase, chemical nature of adsorbate molecules, and alkyl chain length of reversed-phase packing materials. The surface diffusion mechanism in a gaseous system is also likely to be similar to that in liquid-phase adsorption. By taking into account the compensation effect, both activation energy and frequency factor of surface diffusion can be calculated from one datum of surface diffusion coefficient estimated or experimentally measured. Thus the value of surface diffusion coefficient at each given temperature can be estimated by the Arrhenius equation.

The linear free-energy relation holds in reversed-phase liquid chromatography irrespective of the methanol composition in a mobile phase, chemical nature of adsorbate molecules, and alkyl chain length of reversed-phase packing materials. The value of the surface diffusion coefficient can be estimated from the adsorption equilibrium constant estimated or experimentally determined. The results of this study make it possible to apply conventional studies regarding adsorption equilibrium in reversed-phase liquid chromatography to estimation of the surface diffusion coefficient.

The slope of the linear relations suggests that the ratio of E_s/Q_{st} ranges from about 0.3 to 0.6. This result is consistent with the experimental data in gaseous systems and the result obtained by analyzing the relationship between D_s and the ratio of boiling point of adsorbates to experimental temperature. In liquid-phase adsorption, the isosteric heat of adsorption is determined to be smaller than the activation energy of surface diffusion. The difference of thermodynamic properties of adsorption processes in both liquid- and gas-phase systems may result from the solvent effect. By analyzing the correlations between K and D_s and between D_s and T_b , it was also concluded that the value of E_s was smaller than Q_{st} in liquid-phase adsorption as well as in gaseous systems.

On the basis of the results of this study, an estimation method of surface diffusion coefficient in reversed-phase liquid chromatographic systems was proposed. According to the procedures proposed here, the surface diffusion coefficient at each given temperature and amount adsorbed can be estimated from either the physical properties of an adsorbate molecule or the adsorption equilibrium constant.

Nomenclature

a = association coefficient

c = concentration in mobile phase, mmol/cm³

C_e = concentration in effluent, g/cm³
 D = diffusivity, cm²/s
 D_e = intraparticle diffusion coefficient, cm²/s
 D_K = Knudsen diffusivity, cm²/s
 D_m = molecular diffusivity, cm²/s
 d_p = particle diameter, μ m
 D_p = pore diffusivity, cm²/s
 D_s = surface diffusion coefficient, cm²/s
 D_{s0} = frequency factor, cm²/s
 E_s = activation energy of surface diffusion, kJ/mol
 E_z = axial dispersion coefficient, cm²/s
 H = defined in eq 9
 K = adsorption equilibrium constant, cm³/g
 k_f = fluid-to-particle mass-transfer coefficient, cm/s
 k^2 = tortuosity factor of pores
 M = molecular weight, g/mol
 P = pressure, Pa
 q = amount adsorbed, mmol/g
 Q_{st} = isosteric heat of adsorption, kJ/mol
 R = particle radius, μ m
 Re_p = Reynolds number
 R_g = gas constant
 R_p = mean pore radius, cm
 Sc = Schmidt number
 Sh = Sherwood number
 T = temperature, K
 t = time, s
 T_b = boiling point, K
 u_0 = superficial velocity, cm/s
 V = molar volume, cm³/mol
 v = volumetric flow rate, cm³/s
 V_b = molar volume at normal boiling point, cm³/mol
 Ve = volume of pipes, cm³
 w = peak width at half-height, s
 z = longitudinal position in bed, cm

Greek Symbols

δ_0 = defined by eq 3
 δ_{ax} = defined by eq 4
 δ_f = defined by eq 5
 δ_d = defined by eq 6
 ϵ = void fraction in bed
 ϵ_p = porosity
 η = viscosity, Pa·s
 μ_1 = first moment, s
 μ_2' = second moment, s²
 ρ_p = particle density, g/cm³
 σ = collision diameter, cm
 Ω_D = collision function

Subscripts

1 = solute
 2 = solvent
 i, j = components

Appendix

In this study, the contribution of fluid-to-particle mass transfer to the second moment was subtracted when second moments were analyzed by eqs 9 and 10. The external film mass-transfer coefficient, k_f , was estimated by the Wilson-Geankoplis equation for liquid-phase adsorption and the Carberry equation for gaseous systems. The axial dispersion coefficient, E_z , and intraparticle diffusivity, D_e , were determined from the slope and the intercept of a plot of H vs $1/u_0$, respectively. Intraparticle diffusivity is related to both pore diffusivity, D_p , and the surface diffusion coefficient, D_s . The value of D_s was calculated by subtracting the contribution of pore diffusivity to D_e . The value of D_p in liquid-phase adsorption was estimated from the molecular diffusivity, D_m , in a bulk phase,

Table 2. Contributions of Each Mass-Transfer Step to Second Moments^a

adsorbate	column	$\mu_1/(z/u_0)$	$\mu_2'/(2z/u_0)$ (s)	δ_{ax} (%)	δ_f (%)	δ_d (%)
benzene	TMS	1.1	0.13	33.8	21.2	45.0
	C4	1.2	0.19	36.1	21.5	42.5
	C8	1.4	0.28	33.1	24.3	42.7
	ODS	1.7	0.37	25.8	30.0	44.2
naphthalene	TMS	1.2	0.21	29.6	24.2	46.1
	C4	1.5	0.37	30.0	25.7	44.4
	C8	2.2	0.82	31.7	29.3	39.0
	ODS	3.3	1.7	20.6	40.6	38.8
anthracene	TMS	1.5	0.39	27.0	29.6	43.5
	C4	2.0	0.77	29.0	29.7	41.3
	C8	3.9	2.9	28.7	37.3	34.0
	ODS	8.6	11.3	19.5	55.1	25.4

^a Temperature 298 K; $u_0 = 0.12$ cm/s.

porosity of an adsorbent, and tortuosity factor of pores. In gaseous systems, the value of D_p was calculated from Knudsen diffusivity, D_K , instead of D_m in a similar way. The value of D_m was estimated by the Wilke-Chang equation for liquid-phase adsorption and the Hirschfelder equation in gas-phase adsorption.

An uncertainty in the estimation of k_f may influence results of the second moment analysis. First, as described in a previous paper (Miyabe and Suzuki, 1993b), in gaseous adsorption systems the contribution of fluid-to-particle mass-transfer resistance to total resistance was found to be about 1 or 2 orders of magnitude smaller than those of axial dispersion and intraparticle diffusion. For almost all experiments, the contribution of axial dispersion was within 25%, and that of intraparticle diffusion was larger than 75%, suggesting that intraparticle mass-transfer resistance has a significant effect in the ODS column. The uncertainty in the estimation of k_f may not affect the results significantly in gas-phase-adsorption systems.

The contributions of each mass-transfer step in the ODS column, namely axial dispersion, fluid-to-particle mass transfer, and intraparticle diffusion, to second moments is listed in Table 2. As one example, experimental results in liquid-phase adsorption, in which various adsorbates and adsorbents were used, are presented. In liquid-phase adsorption, the contribution of axial dispersion was found to range from 20 to 30%. The contributions of fluid-to-particle mass transfer and intraparticle diffusion were the same order of magnitude. In many cases in this study, the contribution of intraparticle diffusion was larger than that of fluid-to-particle mass transfer, especially under the conditions that the adsorption equilibrium constant was relatively small, that is, the length of an alkyl chain chemically bonded on the surface of silica gel was short and small molecules were used as a sample material. In such cases, the uncertainty in the estimation of k_f may not affect the results significantly. As described in the text, almost all data observed could be plotted around the same line irrespective of experimental conditions. Moreover, the results obtained in liquid-phase adsorption were in good agreement with those in gaseous systems.

According to the equation of Wilson-Geankoplis (eq 11), the value of k_f for benzene at 25 °C was calculated as 0.0185 cm/s under the conditions that the superficial velocity of the mobile phase, that is, methanol/water mixture (70/30 vol %), was about 0.12 cm/s. Another value of k_f was calculated as 0.0148 cm/s under the same conditions by the following equation (Suzuki, 1990).

$$Sh = 1.85[(1 - \epsilon)/\epsilon]^{1/3} Sc^{1/3} Re_p^{1/3} \quad (A1)$$

Both values were of the same order of magnitude. The

Table 3. Contributions of Pore and Surface Diffusions to Intraparticle Diffusion

adsorbate	column	D_e (cm ² /s)	D_p (cm ² /s)	D_e/D_p	D_s (cm ² /s)
benzene	TMS	3.8×10^{-6}	1.2×10^{-6}	3.1	5.4×10^{-6}
	C4	4.3×10^{-6}	1.1×10^{-6}	4.0	4.3×10^{-6}
	C8	4.9×10^{-6}	1.0×10^{-6}	4.8	3.3×10^{-6}
	ODS	5.7×10^{-6}	8.5×10^{-7}	6.7	2.7×10^{-6}
naphthalene	TMS	3.6×10^{-6}	9.5×10^{-7}	3.7	3.5×10^{-6}
	C4	4.1×10^{-6}	8.2×10^{-7}	5.0	2.6×10^{-6}
	C8	5.4×10^{-6}	7.9×10^{-7}	6.9	1.9×10^{-6}
	ODS	7.4×10^{-6}	6.5×10^{-7}	11.3	1.5×10^{-6}
anthracene	TMS	4.1×10^{-6}	7.9×10^{-7}	5.2	2.6×10^{-6}
	C4	4.6×10^{-6}	6.9×10^{-7}	6.6	1.8×10^{-6}
	C8	7.0×10^{-6}	6.5×10^{-7}	10.9	1.2×10^{-6}
	ODS	1.4×10^{-5}	5.5×10^{-7}	25.0	9.6×10^{-7}

relative discrepancy was about 20%. The resulting value of surface diffusion coefficient, D_s , calculated by using k_f estimated by eq A1 was 3.3×10^{-6} cm²/s. By comparison with the original value of D_s , that is, 2.7×10^{-6} cm²/s, the relative error of D_s was about 20%. The tendency of the plots in each figure of this study may not change significantly.

The contributions of pore and surface diffusions to intraparticle diffusion were compared with each other in Table 3. It was elucidated that intraparticle diffusion coefficients were a few times or about 1 or 2 orders of magnitude larger than pore diffusivities. The contribution of surface diffusion to overall mass transfer in reversed-phase packing materials was as much as 75–95% and above. Surface diffusion was dominant for intraparticle diffusion in both gas- and liquid-phase-adsorption systems. It was concluded that the uncertainty in the estimation of D_p has no significant influence on the results of this study.

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