Adsorption 5, 15–24 (1999)

Adsorption Characteristics in Reversed-Phase Liquid Chromatography Using Ethanol/Water Mixed Solvent

KANJI MIYABE, SHIGEYA TAKEUCHI AND YOSHISATO TEZUKA
Chemistry Section, Faculty of Education, Toyama University, Gofuku, Toyama 930, Japan

Abstract. Adsorption characteristics were studied in a reversed-phase liquid chromatography consisting of an octadecylsilyl (ODS)-silica gel and ethanol/water mixture (70/30, v/v), and were compared with corresponding results obtained by using methanol/water and acetonitrile/water mixtures (70/30, v/v) as mobile phase. Similar tendencies were observed for some adsorption characteristics in the three chromatographic systems. However, the magnitude of the characteristics was not entirely identical in the three systems. Surface diffusion was dominant for intraparticle diffusion in the ODS-silica gel particles irrespective of the type of the organic modifiers in mobile phases. A few correlations were confirmed with regard to surface diffusion, i.e., an enthalpy-entropy compensation and a linear free-energy relation. The analogous correlations on surface diffusion phenomena suggest the similarity in the mechanism of surface diffusion in the three chromatographic systems.

Keywords: liquid chromatography, reversed phase, mass transfer, surface diffusion, organic modifier

Introduction

Methanol/water or acetonitrile/water mixtures have frequently been used as mobile phase in reversed-phase liquid chromatography (RPLC). Ethanol and tetrahydrofuran, although not so popular, are sometimes used as organic modifiers in mobile phase. Optimization of mobile phase conditions, i.e., the type and composition of the organic modifiers, is important to establish optimum chromatographic separations. Many studies have been made on the significant influence of the conditions of methanol/water or acetonitrile/water mixtures on the retention behavior in RPLC. However, few studies have been made on RP separations using ethanol/water mixtures. Especially, there are very few or no kinetic studies on mass transfer in RP packing materials.

This paper is concerned with the influence of the type of organic modifiers in mobile phase on adsorption characteristics in RPLC. Adsorption equilibrium, mass transfer rates, and thermodynamic properties were determined by the moment analysis (Suzuki, 1990) of pulse response curves under the conditions that a mixture of ethanol/water (70/30, v/v) and an octadecylsilyl (ODS)-silica gel were used. The results in 70 vol% ethanol were compared with those obtained by using 70 vol% methanol or 70 vol% acetonitrile as mobile phase. It was attempted to analyze surface diffusion coefficient (D_s) in order to get a better understanding for surface diffusion mechanism in RPLC and to develop an estimation procedure of D_s.

Moment Analysis

First absolute moment (μ_1) and second central moment (μ_2') of peaks are expressed as follows.

$$\mu_1 = \int \mathrm{Ce}(t)t\,dt \bigg/ \int \mathrm{Ce}(t)\,dt = (z/u_0)\delta_0 \quad (1)$$

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

$$\delta_0 = \varepsilon + (1-\varepsilon)(\varepsilon_p + \rho_p K) \quad (3)$$

$$\delta_{\mathrm{ax}} = \left(E_z/u_0^2\right)\delta_0^2 \quad (4)$$

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

$$\delta_d = (1-\varepsilon)(R^2/15D_e)(\varepsilon_p + \rho_p K)^2 \quad (6)$$

By Eq. (7), μ_1 was analyzed to determine adsorption equilibrium constant (K).

$$(\mu_1 - t_0)/(1-\varepsilon) = (z/u_0)\rho_p K \tag{7}$$

$$t_0 = (z/u_0)[\varepsilon + (1-\varepsilon)\varepsilon_p] \tag{8}$$

From μ_2', D_s was determined by subtracting the contributions of some mass transfer processes in a column. A parameter H was calculated as follows.

$$H = \left(\mu_2'/\mu_1^2\right)(z/2u_0) = \left(E_z/u_0^2\right) + H_0 \tag{9}$$

$$H_0 = \delta_f\big/\delta_0^2 + \delta_d\big/\delta_0^2 \tag{10}$$

Axial dispersion coefficient (E_z) and intraparticle diffusivity (D_e) can be determined from the slope and intercept of the plot between H vs. $1/u_0$. The value of δ_f was calculated from Eq. (5) and its contribution to μ_2' was corrected. Fluid-to-particle mass transfer coefficient (k_f) was estimated by the equation of Wilson-Geankoplis (1966).

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

Molecular diffusivity (D_m) of a solute in the ethanol/water mixture was estimated by the Wilke-Chang equation (Reid et al., 1977).

$$D_m = 7.4 \times 10^{-8}(\alpha_{\mathrm{sv}}M_{\mathrm{sv}})^{1/2}T\big/\left(\eta_{\mathrm{sv}}V_{b,s}^{0.6}\right) \tag{12}$$

The contribution of adsorption rate at an adsorption site to μ_2' was assumed to be negligibly small. The value of D_e is related to both pore diffusivity (D_p) and D_s as follows.

$$D_e = D_p + \rho_p K D_s \tag{13}$$

The value of D_s was determined by subtracting the contribution of D_p to D_e. According to the parallel pore model, D_p was estimated from D_m, ε_p, and tortuosity factor (k) of pores.

$$D_p = (\varepsilon_p/k^2)D_m \tag{14}$$

The value of k was determined by pulse response experiments using a nonadsorbable substance, i.e., uracil.

The values of μ_1 and μ_2' of peaks were calculated by the equations (Foley and Dorsey, 1983).

$$\mu_1 = t_G + \tau \tag{15}$$

$$\mu_2' = W_{0.1}^2\big/[1.764(B/A)^2 - 11.15(B/A) + 28] \tag{16}$$

$$t_G = t_R - \sigma_G[-0.193(B/A)^2 + 1.162(B/A) - 0.545] \tag{17}$$

$$\sigma_G = W_{0.1}/[3.27(B/A) + 1.2] \tag{18}$$

$$\tau = \left(\mu_2' - \sigma_G^2\right)^{0.5} \tag{19}$$

Peak width ($W_{0.1}$) and empirical asymmetry factor (B/A) at 10% of peak height were measured. The value of B/A represents the ratio of peak width in the rear part of a peak to that in the front part. In this study, B/A ranged from 1.01 to 1.10, indicating that chromatographic peaks were not so asymmetry. It has been pointed out that nonlinearity of adsorption isotherm is not only one source of peak asymmetry in chromatography (Giddings, 1965; Guiochon et al., 1994). Several factors, other than nonlinearity of adsorption isotherm, such as heterogeneity of the surface of stationary phase, coexistence of fast and slow mass transfer processes, and large volumes of dead space within a column or a detection unit, also cause asymmetry peaks. The influence of skewed profile of chromatographic peaks on the results of the moment analysis in this study was eliminated by applying the above equations proposed by Foley and Dorsey. The effects of μ_1 and μ_2' of pulses introduced at the inlet of the column were neglected because the pulse size was extremely small.

Experimental

Apparatus

A high performance liquid chromatograph equipment (LC-6A, Shimadzu) was used. A small volume of sample solutions were introduced into a fluid flow by using a sample injector. A thermostatted water bath was used to maintain column temperature constant. The concentration of solutes was monitored by an ultraviolet detector.

Column and Reagents

Several properties of an ODS column (YMC) are shown in Table 1. The fraction of ethanol in mobile phase was selected as a typical composition. The concentration of sample solutions was about 0.1 wt% in 70 vol% ethanol, and injection volume was several μl each. The concentration and injection volume of uracil

Table 1. Properties of a column and experimental conditions.

Average particle diameter, d_p (μm)	45
Particle density, ρ_p (g cm^{-3})	0.83
Porosity, ε_p	0.47
Tortuosity factor, k^2	3.6
Carbon content (wt%)	17.1
Column size	150 mm × 6 mm I.D.
Void fraction, ε	0.40
Peclet number, Pe	1.1–1.2
Column temperature	288–308 (K)
Mobile phase	Ethanol/water: 70/30 (v/v)
Superficial velocity, u_0 (cm s^{-1})	0.05–0.12
Sample material	Benzene derivatives, naphthalene

solution were 0.01 wt% in 70 vol% ethanol and 0.5 μl, respectively. The concentration of the solute injected into the ODS column decreased with band spreading in the progress of chromatographic separation. The height of chromatographic peaks were calculated to be of the order of 10^{-8}–10^{-5} g cm^{-3} by assuming a Gaussian peak. It has also been confirmed that slight changes in the concentration and injection volume of the sample solutions provide no influence on the peak retention. It was concluded that experimental data could be analyzed based on linear adsorption assumption.

Results and Discussion

First Moment Analysis

According to the van't Hoff equation, ln K was plotted against $1/T$ in Fig. 1.

$$K = K_0 \exp(-Q_{\text{st}}/R_g T) \qquad (20)$$

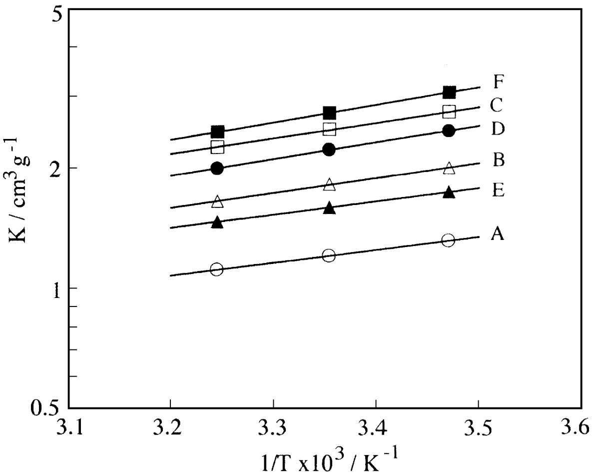

Figure 1. Van't Hoff plot of adsorption equilibrium constant. Solute: A, benzene; B, toluene; C, ethylbenzene; D, naphthalene; E, chlorobenzene; F, *p*-xylene.

Resulting values of $-Q_{\text{st}}$ listed in Table 2 are ranging from 6.3 to 8.5 kJ mol^{-1}. The values are of the same order of magnitude compared with the other experimental results previously reported (Colin et al., 1978; Colin and Guiochon, 1977, 1978; Horvath and Melander, 1977; Issaq and Jaroniec, 1989; Knox and Vasvari, 1973; Majors and Hopper, 1974), and are comparable to or smaller than those in 70 vol% methanol, i.e., 6.7–10.3 kJ mol^{-1} (Miyabe and Suzuki, 1995b). In comparison with corresponding results in 70 vol% acetonitrile, i.e., 5.8–7.1 kJ mol^{-1} (Miyabe and Takeuchi, 1997a), larger values of $-Q_{\text{st}}$ were obtained in 70 vol% ethanol. The value of K_0 represents the entropy change arising from adsorption of a solute. Adsorption process was accompanied by the reduction of entropy in each adsorption system.

Figure 2 illustrates the correlations of K with hydrocarbonaceous surface area (A) of the solutes. The magnitude of K was in the order: in 70 vol% methanol > in

Table 2. Thermodynamic properties in liquid phase adsorption.

Solute	$-Q_{\text{st}}$ (kJ mol^{-1})	K_0 (cm^3 g^{-1})	E_s (kJ mol^{-1})	D_{s0} (cm^2 s^{-1})
Benzene	6.3	0.097	16.4–18.6 (18.3)*	1.5×10^{-3}–3.5×10^{-3} (3.1×10^{-3})*
Toluene	7.2	0.10	18.5–20.5 (18.9)	3.0×10^{-3}–6.6×10^{-3} (3.5×10^{-3})
Ethylbenzene	7.6	0.12	15.6–19.5 (17.7)	7.8×10^{-4}–3.7×10^{-3} (1.8×10^{-3})
Naphthalene	8.0	0.086	20.3–23.3 (22.0)	4.3×10^{-3}–1.4×10^{-2} (8.5×10^{-3})
Chlorobenzene	6.4	0.12	17.1–19.9 (18.9)	1.7×10^{-3}–5.1×10^{-3} (3.5×10^{-3})
p-Xylene	8.5	0.089	15.1–18.1 (17.0)	5.9×10^{-4}–2.0×10^{-3} (1.3×10^{-3})

*The values in parentheses were determined as appropriate values.

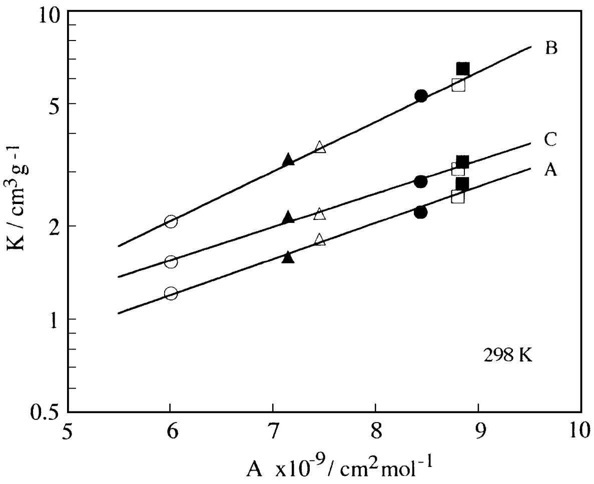

Figure 2. Correlation of adsorption equilibrium constant with hydrocarbonaceous surface area of solutes. Organic modifier: A, ethanol; B, methanol; C, acetonitrile. Symbols: refer to Fig. 1.

70 vol% acetonitrile > in 70 vol% ethanol. The value of A was calculated by summing surface area increments of each group in a molecule (Bondi, 1964). Figure 2 shows three linear relations between $\ln K$ and A according to the type of organic modifiers. The slopes of the straight lines were analyzed by applying the solvophobic theory. In the theory, it is assumed that the contact area between polar solvents and the hydrophobic surfaces of both solute molecules and the ODS ligands decreases when the solute molecules are retained on the ODS ligands, and that the reduction of the hydrophobic surface area (ΔA) is proportional to the surface area of the solute (A_s). The free energy change due to the retention in liquid phase system (ΔG_{liq}) is represented as follows.

$$\begin{aligned}\Delta G_{\text{liq}} = {} & \Delta G_{\text{gas}} - \Delta G_{\text{vdw},s} + N_A(\lambda - 1) \\ & \times \mu_s^2 \Psi P \big/ (2\lambda v_s) - N_A \Delta A - N_A A_s(\kappa^e - 1) \\ & \times V^{2/3}\gamma \big/ V_s^{2/3} - R_g T \ln(R_g T / P_0 V) \qquad (21)\end{aligned}$$

The contribution of the electrostatic term (the third term on the right-hand side (RHS) of Eq. (21)) to ΔG_{liq} was assumed to be negligible in the case of hydrophobic interaction. Retention factor (k') is related to ΔG_{liq} by considering a phase ratio of both stationary and mobile phases (F_R).

$$\Delta G_{\text{liq}} = -R_g T(\ln k' - \ln F_R). \qquad (22)$$

From Eqs. (21) and (22), k' can be expressed by assuming that the shape of the solute is spherical.

$$\begin{aligned}\ln k' = {} & \ln F_R - \Delta G_{\text{gas}}/R_g T + \Delta G_{\text{vdw},s}/R_g T \\ & + N_A \Delta A \gamma / R_g T + 4.836 N_A^{1/3}(\kappa^e - 1) \\ & \times V^{2/3}\gamma / R_g T + \ln(R_g T / P_0 V) \qquad (23)\end{aligned}$$

The values of the first, fifth, and sixth terms on the RHS of Eq. (23) are constant irrespective of the type of solutes. According to Eq. (23), Horvath et al. (1976) estimated the ratio of $\Delta A / A_s$ for three kinds of homologies from the slope of linear correlations between $\ln k'$ and A_s by assuming that the changes in the second and third terms on the RHS of Eq. (23) very nearly cancel each other.

Similarly, $\Delta A/A$ was calculated as about 0.26 in 70 vol% ethanol from the slope of the linear correlation in Fig. 2. Corresponding values of $\Delta A/A$ were about 0.3–0.35 in 70 vol% methanol (Miyabe and Suzuki, 1995a), and 0.18 in 70 vol% acetonitrile (Miyabe and Takeuchi, 1997a). Though mobile phase compositions were not entirely identical, similar values of $\Delta A/A$ were reported as 0.35 (Horvath et al., 1976) and 0.2–0.3 (Belfort et al., 1984). It is indicated that the magnitude of the interaction between solute molecules and ODS ligands may be in the order: in 70 vol% methanol > in 70 vol% ethanol > in 70 vol% acetonitrile. This order is identical with that for Q_{st}, however, is different from that for K.

Second Moment Analysis

The contributions of each mass transfer process in the ODS column to μ_2' are compared in Table 3. The contributions of axial dispersion (δ_{ax}) and fluid-to-particle mass transfer (δ_f) are ranging in about 12–23% and 23–37%, respectively. The contribution of intraparticle diffusion (δ_d) is found to be ranging in about 49–59%. The contribution of δ_d probably decreases with an increase in K and temperature. It was confirmed that the contribution of intraparticle diffusion had an important role for overall mass transfer resistance in the ODS column when the size of the adsorbent particle was relatively large.

Table 4 shows that D_e is a few times or about one order of magnitude larger than D_p. The contribution of the surface diffusion to mass transfer in the ODS-silica gel was about 78–90%. The value of D_s was calculated to be of the order of 10^{-6} cm^2 s^{-1}.

Table 3. Comparison of the contributions of axial dispersion, fluid-to-particle mass-transfer, and intraparticle diffusion to second moment.

Solute	T (K)	μ_1 (z/u_0)	μ_2' $(2z/u_0)$ (s)	δ_{ax} (%)	δ_f (%)	δ_d (%)
Benzene	288	1.35	0.39	15.1	25.7	59.2
	298	1.30	0.30	19.0	23.9	57.1
	308	1.23	0.22	22.8	22.6	54.6
Toluene	288	1.68	0.66	14.5	30.9	54.5
	298	1.59	0.48	18.1	28.9	53.0
	308	1.50	0.35	21.4	27.1	51.5
Ethylbenzene	288	2.06	1.04	13.9	35.0	51.1
	298	1.94	0.75	17.1	32.6	50.3
	308	1.79	0.54	19.6	30.3	50.1
Naphthalene	288	1.92	1.04	12.2	30.1	57.8
	298	1.80	0.73	15.1	28.7	56.2
	308	1.67	0.50	19.0	27.3	53.7
Chlorobenzene	288	1.55	0.57	14.3	28.5	57.3
	298	1.49	0.43	17.8	27.0	55.2
	308	1.42	0.33	21.5	25.2	53.3
p-Xylene	288	2.22	1.20	13.5	36.5	50.0
	298	2.06	0.83	17.2	33.8	49.0
	308	1.90	0.60	18.7	31.1	50.2

$u_0 = 0.12$ cm s^{-1}.

Table 4. Comparison of the contributions of pore and surface diffusions to intraparticle diffusion.

Solute	T (K)	D_e (cm^2 s^{-1})	D_p (cm^2 s^{-1})	D_e/D_p	D_s (cm^2 s^{-1})	$\rho_p K D_s/\varepsilon_p D_p^*$
Benzene	288	2.1×10^{-6}	4.5×10^{-7}	4.8	1.5×10^{-6}–1.6×10^{-6} (1.5×10^{-6})**	7.7
	298	2.6×10^{-6}	6.4×10^{-7}	4.1	1.9×10^{-6}–2.0×10^{-6} (2.0×10^{-6})	6.6
	308	3.2×10^{-6}	9.0×10^{-7}	3.6	2.5×10^{-6}	5.4
Toluene	288	2.6×10^{-6}	4.0×10^{-7}	6.5	1.3×10^{-6}	11.4
	298	3.2×10^{-6}	5.7×10^{-7}	5.6	1.6×10^{-6}–1.8×10^{-6} (1.7×10^{-6})	9.5
	308	3.8×10^{-6}	7.9×10^{-7}	4.8	2.2×10^{-6}	8.1
Ethylbenzene	288	2.9×10^{-6}	3.6×10^{-7}	8.1	1.1×10^{-6}–1.2×10^{-6} (1.1×10^{-6})	14.8
	298	3.5×10^{-6}	5.1×10^{-7}	6.8	1.4×10^{-6}	12.0
	308	4.1×10^{-6}	7.1×10^{-7}	5.7	1.8×10^{-6}	10.0
Naphthalene	288	2.2×10^{-6}	3.5×10^{-7}	6.2	8.7×10^{-7}–9.1×10^{-7} (8.8×10^{-7})	10.9
	298	2.7×10^{-6}	5.0×10^{-7}	5.4	1.2×10^{-6}–1.3×10^{-6} (1.2×10^{-6})	9.3
	308	3.3×10^{-6}	6.9×10^{-7}	4.8	1.6×10^{-6}	8.1
Chlorobenzene	288	2.3×10^{-6}	4.1×10^{-7}	5.7	1.3×10^{-6}	9.7
	298	2.9×10^{-6}	5.8×10^{-7}	4.9	1.7×10^{-6}–1.9×10^{-6} (1.7×10^{-6})	8.2
	308	3.5×10^{-6}	8.1×10^{-7}	4.3	2.1×10^{-6}–2.2×10^{-6} (2.2×10^{-6})	7.0
p-Xylene	288	3.1×10^{-6}	3.6×10^{-7}	8.7	1.1×10^{-6}	16.5
	298	3.7×10^{-6}	5.1×10^{-7}	7.3	1.4×10^{-6}–1.5×10^{-6} (1.4×10^{-6})	13.2
	308	4.2×10^{-6}	7.1×10^{-7}	5.8	1.6×10^{-6}–1.7×10^{-6} (1.7×10^{-6})	10.3

*The values were calculated from appropriate values of D_s.

**The values in parentheses were determined as appropriate values.

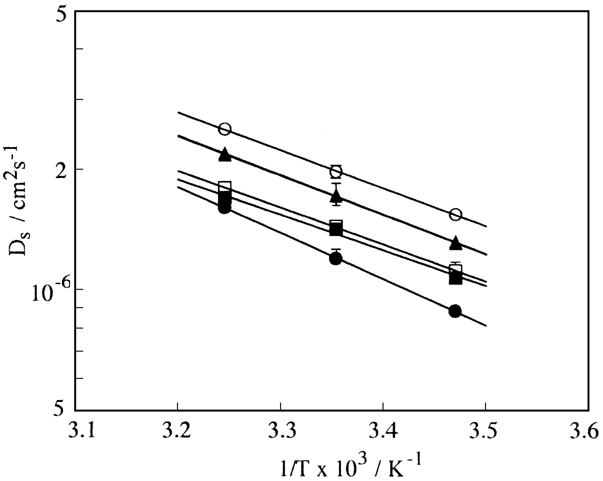

Figure 3. Arrhenius plot of surface diffusion coefficient. Symbols: refer to Fig. 1.

Yoshida et al. (1994) made an extremely thorough and complete investigation on the parallel transport of bovine serum albumin by surface and pore diffusion in porous chitosan ion exchangers and proposed a sufficiently effective and reliable theoretical approach for determining surface and pore diffusivities in porous materials. They claimed that the degree of the contribution of surface and pore diffusions to intraparticle diffusion must be judged from $\rho_p q D_s/\varepsilon_p c D_p$. Because pulse response experiments were made under linear adsorption equilibrium conditions in this study, the ratio q/c is equal to K. Most values of $\rho_p K D_s/\varepsilon_p D_p$ indicated in Table 4 are about 10 or above, suggesting that surface diffusion has a dominant role for intraparticle diffusion in the ODS-silica gel particles as expected from D_e/D_p.

According to Arrhenius plots in Fig. 3, E_s in 70 vol% ethanol was determined.

$$D_s = D_{s0}\exp(-E_s/R_g T) \qquad (24)$$

As listed in Table 2, E_s is ranging from 17 to 22 kJ mol^{-1}, which is intermediate value compared with corresponding results in 70 vol% methanol, i.e., 19–23 kJ mol^{-1} (Miyabe and Suzuki, 1995b) and those in 70 vol% acetonitrile, i.e., 14–17 kJ mol^{-1} (Miyabe and Takeuchi, 1997a). This correlation is consistent with the results concerning Q_{st} and $\Delta A/A$ in the three mobile phases, suggesting that the adsorptive interaction between solutes and the surface of the ODS-silica gel is in the order: in 70 vol% methanol > in 70 vol% ethanol > in 70 vol% acetonitrile.

As shown in Table 2, E_s was larger than $-Q_{\mathrm{st}}$ when 70 vol% ethanol was used. Similar experimental results have already been reported for surface diffusion phenomena in liquid phase adsorption (Awum et al., 1988; Ching et al., 1989; Ma et al., 1988; Miyabe and Suzuki, 1992, 1993b, 1994b, 1995a, b, 1997a). However, very few interpretations have been proposed for the correlation between E_s and Q_{st}. It seems to be energetically advantageous for adsorbed molecules to be desorbed from a surface to a bulk phase rather than to migrate on the surface under the conditions that E_s is larger than $-Q_{\mathrm{st}}$. The presence of surface diffusion phenomena is denied in such cases. The authors attempted to quantitatively explain by the solvophobic theory that the results were attributed to solvation of solutes in liquid phase (Miyabe and Suzuki, 1992, 1995a), and also proposed a restricted molecular diffusion model as one approximation for surface diffusion mechanism. A formulation of D_s was derived on the basis of the absolute rate theory. A quantitative interpretation could be provided for $E_s/(-Q_{\mathrm{st}})$ larger than unity by the restricted molecular diffusion model for surface diffusion (Miyabe and Takeuchi, 1997b). Both temperature and concentration dependence of D_s in various liquid phase adsorption systems were consistently interpreted by the model (Miyabe and Takeuchi, 1997c).

Enthalpy-Entropy Compensation Effect

Figure 4 shows the correlation between E_s and D_{s0} obtained from the Arrhenius plot in Fig. 3. The causes of the error concerning the determination of D_s are divided into two categories. One is some corrections for the contributions of mass transfer processes in the ODS column and packing materials to peak spreading. In this study, the corrections were made in order to determine D_s from μ_2'. However, the error from the corrections is not so large and about several percent or less for E_s and D_{s0} as well as D_s because the direction of change in D_s is same for all plots in Fig. 3. This type of error only brings about almost parallel changes to the correlations between D_s and some adsorption parameters and has little influence on the conclusions in this study. Therefore, corresponding error bars were eliminated in Figs. 3–5. The other is the variance of experimental data. The magnitude of the error for the determination of D_s is also a degree of about several percent. However, percent errors for E_s and D_{s0} are larger than that for D_s because the direction of change

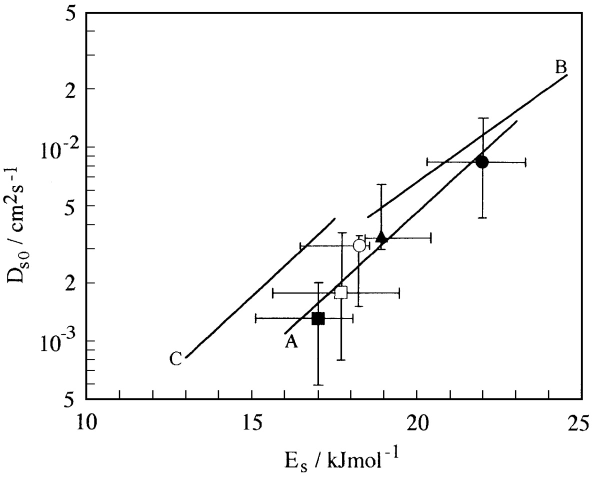

Figure 4. Correlation of frequency factor with activation energy of surface diffusion. Organic modifier: A, ethanol; B, methanol; C, acetonitrile. Symbols: refer to Fig. 1.

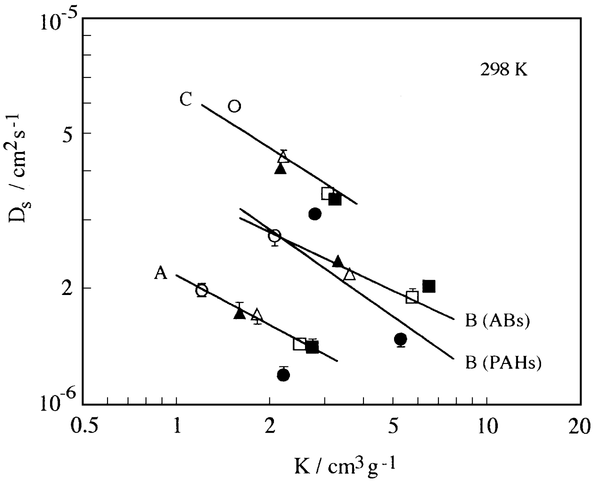

Figure 5. Correlation of surface diffusion coefficient with adsorption equilibrium constant. Organic modifier: A, ethanol; B, methanol; C, acetonitrile. Solute: ABs, *n*-alkylbenzene; PAHs, polyaromatic hydrocarbon. Symbols: refer to Fig. 1.

in D_s is not systematic. Horizontal and vertical lines on the plots in Fig. 4 represent ranges of E_s and D_{s0} between the two extremes. However, E_s and D_{s0} change in a systematic manner, that is, another is also large (small) when one is large (small). Though the errors for E_s and D_{s0} are not negligible as illustrated in Fig. 4, the resulting linear correlation (line A) between E_s and D_{s0} may not be significantly changed. Plots for each solute in 70 vol% ethanol scattered around the straight line A, indicating that the enthalpy-entropy compensation effect was established. It is expected that both D_{s0} and E_s can be calculated from one datum of D_s estimated or measured. At a given temperature, D_s can be estimated by the Arrhenius equation.

Figure 4 also illustrates linear correlations between D_{s0} and E_s for the solutes in the RPLC using 70 vol% methanol (Miyabe and Suzuki, 1994a) and 70 vol% acetonitrile (Miyabe and Takeuchi, 1997d). Plots on the lines B and C are eliminated because it seems to be important to confirm straight correlations between E_s and D_{s0} rather than to compare each plot. Though the three lines are not completely identical, the tendency of the correlations was similar to each other. This result leads to the conclusion that the mechanism of surface diffusion is essentially similar in the RPLC systems using the three mobile phase solvents.

Linear Free-Energy Relation

A linear free-energy relation can be expected to hold when the enthalpy-entropy compensation effect is established. Figure 5 shows a linear correlation between $\ln D_s$ and $\ln K$ in the ODS-silica gel and 70 vol% ethanol system. Figure 5 also shows the correlations between $\ln D_s$ and $\ln K$ in 70 vol% methanol and 70 vol% acetonitrile. Different lines were observed for alkylbenzenes (ABs) and polyaromatic hydrocarbons (PAHs) when 70 vol% methanol was used. Similar tendencies between $\ln D_s$ and $\ln K$ were observed in the three mobile phase systems.

Figure 5 indicates that D_s for the solutes are in the order: in 70 vol% acetonitrile > in 70 vol% methanol > in 70 vol% ethanol and that surface diffusion phenomena are influenced by the conditions of mobile phase. The order for D_s is inconsistent with the results relating to K, $\Delta A/A$, Q_{st}, and E_s. A consistent interpretation has not been yet reported for the role of mobile phase solvents on the retention, mass transfer rates, and thermodynamic properties in RPLC.

The slope of the linear relations in Fig. 5 is equal to $E_s/(-Q_{\mathrm{st}})$. It is indicated that $E_s/(-Q_{\mathrm{st}})$ in the RPLC systems ranges from about 0.4 to 0.7. This result is consistent with the experimental data in gaseous systems (Miyabe and Suzuki, 1993a). Mitani et al. (1972) also studied linear correlation between $\ln D_s$ and a Henry constant in various gas phase adsorption systems using several kinds of adsorbates and adsorbents, and reported that $E_s/(-Q_{\mathrm{st}})$ was found to range from about 0.3 to 1.0. In this study, it was concluded by analyzing the correlations between $\ln D_s$ and $\ln K$

that E_s was smaller than $-Q_{\mathrm{st}}$ in the RPLC systems as well as in gas phase adsorption.

It was confirmed that the linear free-energy relation held in the RPLC irrespective of the type of the organic modifiers in mobile phase. The value of D_s can be calculated from K estimated or experimentally measured according to the correlations. In the field of RPLC, the retention behavior has been extensively studied on the basis of various theories such as the extended solubility parameter model, the lattice statistical thermodynamic theory, the solvophobic theory, and the quantitative structure-retention relationships. The value of K can be approximated by the theories. The results in Fig. 5 make it possible to apply the results of the conventional studies regarding the retention behavior to the estimation of D_s in RPLC. From D_s experimentally determined or estimated by the above procedures, D_s at a given temperature can be calculated by considering the enthalpy-entropy compensation effect of surface diffusion phenomena.

Conclusion

Adsorption characteristics in RPLC were studied by pulse response method and moment analysis. The ODS-silica gel and 70 vol% ethanol were used as stationary and mobile phase. Some items of information about adsorption equilibrium, mass transfer rates, and thermodynamic properties were obtained. Surface diffusion had a significant role for intraparticle diffusion in the ODS-silica gel. It was attempted to analyze characteristic features of surface diffusion. The establishment of the enthalpy-entropy compensation effect and the liner free-energy relation were confirmed.

The results were compared with those determined in RPLC systems consisting of an ODS-silica gel and 70 vol% methanol or 70 vol% acetonitrile. Though the magnitude of some adsorption characteristics in the three mobile phase solvents were not identical, adsorption mechanism is probably analogous in the three systems because similar tendencies were observed for the adsorption characteristics.

Nomenclature

A	hydrocarbonaceous surface area	$\mathrm{cm^2\ mol^{-1}}$
ΔA	reduction in hydrocarbonaceous surface area due to adsorption	$\mathrm{cm^2\ mol^{-1}}$
c	concentration	$\mathrm{g\ cm^{-3}}$
Ce	peak profile as a function of t	—
D_e	intraparticle diffusion coefficient	$\mathrm{cm^2\ s^{-1}}$
D_m	molecular diffusivity	$\mathrm{cm^2\ s^{-1}}$
D_p	pore diffusivity	$\mathrm{cm^2\ s^{-1}}$
d_p	particle diameter	cm
D_s	surface diffusion coefficient	$\mathrm{cm^2\ s^{-1}}$
D_{s0}	frequency factor	$\mathrm{cm^2\ s^{-1}}$
E_s	activation energy of surface diffusion	$\mathrm{kJ\ mol^{-1}}$
E_z	axial dispersion coefficient	$\mathrm{cm^2\ s^{-1}}$
F_R	phase ratio	—
ΔG	Gibbs free energy change	$\mathrm{kJ\ mol^{-1}}$
K	adsorption equilibrium constant	$\mathrm{cm^3\ g^{-1}}$
K_0	adsorption equilibrium constant at $1/T = 0$	$\mathrm{cm^3\ g^{-1}}$
k	tortuosity factor	—
k'	retention factor	—
k_f	fluid-to-particle mass transfer coefficient	$\mathrm{cm\ s^{-1}}$
M	molecular weight	—
N_A	Avogadro number	$\mathrm{mol^{-1}}$
Pe	Peclet number	—
P_0	atmospheric pressure	Pa
q	amount adsorbed	$\mathrm{g\ g^{-1}}$
Q_{st}	isosteric heat of adsorption	$\mathrm{kJ\ mol^{-1}}$
R	particle radius	cm
Re_p	Reynolds number	—
R_g	gas constant	$\mathrm{kJ\ mol^{-1}\ K^{-1}}$
Sc	Schmidt number	—
Sh	Sherwood number	—
T	temperature	K
t	time	s
t_G	defined by Eq. (17)	—
t_R	retention time	s
u_0	superficial velocity	$\mathrm{cm\ s^{-1}}$
V	molar volume	$\mathrm{cm^3\ mol^{-1}}$
V_b	molar volume at normal boiling point	$\mathrm{cm^3\ mol^{-1}}$
$W_{0.1}$	peak width at 10% of height	s
z	longitudinal position in bed	cm
α	association coefficient	—
δ_{ax}	contribution of axial dispersion to overall mass transfer resistance	—
δ_f	contribution of fluid-to-particle mass transfer to overall mass transfer resistance	—

δ_d	contribution of intraparticle diffusion to overall mass transfer resistance	—
ε	void fraction in bed	—
ε_p	porosity	—
γ	surface tension	$N\ m^{-1}$
η	viscosity	Pa s
κ^e	energy correction for curved surface	
λ	ratio of the molecular volume of a complex consisting of a solute and ODS ligand to ν_s	—
μ_1	first absolute moment	s
μ_2'	second central moment	s^2
μ	dipole moment	cm
ν	molecular volume	cm^3
ρ_p	particle density	$g\ cm^{-3}$
σ_G	defined by Eq. (18)	—
τ	defined by Eq. (19)	—

Subscripts

gas	gas phase
liq	liquid phase
s	solute
sv	solvent
vdw	van der Waals interaction

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