Chromatography of Liquid-Phase Adsorption on Octadecylsilyl-Silica Gel

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Intraparticle diffusion and adsorption equilibrium on octadecylsilyl-silica gel (ODS) were studied. As an adsorbate, p-tert-octylphenol (PTOP) was employed. The intraparticle diffusion coefficient was measured by the chromatographic technique and the moment analysis at zero and several surface coverages. Adsorption isotherms can be correlated by the Langmuir equation. The isosteric heat of adsorption and the activation energy of surface diffusion were constant regardless of the amount adsorbed. These results suggest that ODS has an energetically homogeneous surface. The effect of solvent on isosteric heat of adsorption in the liquid system was discussed qualitatively by the solvophobic theory. Surface diffusion coefficient of PTOP on ODS was of the order of 10^{-7} *to* 10^{-6} cm^2/s. *Surface diffusion was dominant for the intraparticle diffusion in ODS, and its coefficient increased with an increase in the amount adsorbed. Positive concentration dependence of the surface diffusion coefficient was interpreted in terms of diffusion by potential chemical driving force.*

Introduction

High-performance liquid chromatography (HPLC) is gaining popularity as one of the most powerful tools for separation and purification of objective components in mixtures. In the field of analytical liquid chromatography, the reversed-phase technique is most frequently employed. It is estimated that 60–80% of chromatographic separation on analytical works has been carried out in a reversed-phase mode. Among reversed-phase packing materials, ODS is the most effective and widely used. Consequently, most of analytical separations by HPLC are made by use of ODS as an adsorbent.

Recently considerable attention has been paid for the use of HPLC and/or LC on a large, preparative scale (Verzele and Geereart, 1980; Bidlingmeyer, 1987), as well as an analytical purpose in connection with the development of biological, fine chemical and their related technologies. There have been many studies on the theory and practice of a preparative LC. As a result, characteristics of a large, preparative-scale separation, which differ considerably from those of an analytical procedure, have been elucidated theoretically. A number of materials such as biologically active substances, pharmaceuticals and chemicals have been purified by a preparative LC. Several modes of LC are used in preparative separations, and the role of reversed-phase technique has become progressively important. Practical applications of reversed-phase LC, in which ODS is mainly employed, to industrial-scale separations have also been reported (Cantwell et al., 1984; Kroeff et al., 1989; Miyabe et al., 1989).

Study of the mass transfer rate and adsorption equilibrium is important in understanding and designing such large-scale processes of chromatography. The diffusion resistance in adsorbent particles seems to have a significant effect on the overall adsorption rate and consequently on the efficiency of a chromatographic separation. Intraparticle diffusion in many porous adsorbents has been studied by several methods such as batch adsorption (Suzuki and Kawazoe, 1975; Suzuki et al., 1976), chromatographic technique (Schneider and Smith, 1968; Kawazoe et al., 1974; Chihara et al., 1978; Awum et al., 1988), and steady-state experiment (Suzuki and Fujii, 1982; Takeuchi et al., 1984). It is well established that in many cases surface diffusion has a more important role than pore diffusion for

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the intraparticle diffusion. The surface diffusion coefficient shows positive concentration dependence on the amount adsorbed. In spite of the extensive applications of reversed-phase HPLC and/or LC with ODS, little is known on the intraparticle diffusion in ODS.

In a preparative LC, chromatographic separations are often operated under mass overload conditions unlike analytical procedure. The development of a preparative LC is accompanied by additional problems such as nonlinearity of adsorption isotherm and concentration dependence of diffusivity.

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 surface diffusion coefficient has been explained by the change in adsorption energy. Komiyama and Smith (1974) correlated surface diffusion coefficient to the adsorption equilibrium constant. Neretnieks (1976) discussed a decrease in the heat of adsorption with an increase in the amount adsorbed in the case of the Temkin isotherm and suggested an exponential function of the adsorbed-phase concentration. Sudo et al. (1978) related surface diffusion coefficient to the final amount adsorbed to explain the concentration dependence. Suzuki and Fujii (1982) determined surface diffusion coefficient by the Wicke-Kallenbach-type steady-state diffusion experiment. Strong concentration dependence of the surface diffusion coefficient on the amount adsorbed was interpreted in terms of the change in the heat of adsorption with surface coverage for the Freundlich isotherm system. Moon and Lee (1983) suggested an empirical equation of the time-average amount adsorbed. Many studies on the concentration dependence of surface diffusion coefficient were made on liquid-phase adsorption systems, where activated carbon was mainly used as an adsorbent (Muraki et al., 1982). However, no data are available on the concentration dependence of the surface diffusion coefficient in ODS.

This article is concerned with characteristics of liquid-phase adsorption on the surface of ODS. Adsorption equilibrium constants and surface diffusion coefficient of PTOP were determined at various surface coverages in the range from 278 to 308 K by the breakthrough and chromatographic methods. A concentration pulse of PTOP was introduced to a fluid flow at the inlet of a column. Response curves observed were analyzed by the moment method. Thermodynamic parameters of liquid-phase adsorption on ODS were determined. An attempt was also made to interpret the effect of solvent on the isosteric heat of adsorption by applying the solvophobic theory. Mass-transport behavior in ODS column and concentration dependence of the surface diffusion coefficient were studied. For a nonadsorbable substance, uracil, chromatographic measurements were made in the same way.

Moment Analysis of Chromatographic Data (Suzuki, 1973, 1990)

A small perturbation pulse of a solute was injected to the steady flow of mobile phase. Chromatographic data observed were analyzed by the moment method. In this study, we analyzed the contributions of each mass-transport step in a column: the axial dispersion, the fluid-to-particle mass transfer, and the intraparticle diffusion to adsorption/desorption rate of adsorbates. We assumed that both pore diffusion and surface diffusion contributed to the intraparticle diffusion.

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

$$\mu_1 = \int_0^\infty Ce(t)t\,dt \bigg/ \int_0^\infty Ce(t)\,dt = (z/u_0)\delta_0 \tag{1}$$

$$\mu_2' = \int_0^\infty Ce(t)(t-\mu_1)^2 dt \bigg/ \int_0^\infty Ce(t)\,dt = (2z/u_0)(\delta_{ax} + \delta_f + \delta_d) \tag{2}$$

where

$$\delta_0 = \epsilon + (1-\epsilon)(\epsilon_p + \rho_p K) \tag{3}$$

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

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

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

The first moment is analyzed by Eq. 7 derived from Eq. 1 as:

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

where

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

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

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

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

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

The value of δ_f was calculated from Eq. 5, and its contribution to the second moment was corrected. External mass-transfer coefficient, k_f, was calculated by the equation of Wilson-Geankoplis:

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

Molecular diffusivity, Dm, of a solute in methanol-water mixture was estimated by the Wilke-Chiang equation:

$$Dm = 7.4 \times 10^{-8}(a_2M_2)^{1/2}T/\eta_2 V_1^{0.6} \tag{12}$$

The contribution of the 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, Ez, and effective intraparticle diffusion coefficient, De, from the slope and the intercept, respectively. The effective intraparticle diffusion coefficient is related to both pore diffusivity, Dp, and surface diffusion coefficient, Ds, as:

$$De = Dp + \rho_p KDs \tag{13}$$

When the elution peak can be approximated by the normal distribution curve, the first and second moments can be determined from the position and the width of a peak, respectively. Figure 1 shows examples of chromatographic peaks of PTOP for zero surface coverage at different temperatures. The experimental first absolute moment, $\mu_{1\,\mathrm{exp}}$, includes the effects of the volume, Ve, of the pipes between an injector and a column and that between a column and a detector. The correction of the extra column volume was made for $\mu_{1\,\mathrm{exp}}$ as:

$$\mu_1 = \mu_{1\,\mathrm{exp}} - Ve/v \tag{14}$$

The second moment was calculated from a peak width at half height, w, by:

$$\mu_2' = w^2/5.54 \tag{15}$$

The contribution of the pipes to the second moment was measured by the chromatographic method without a column and was corrected. The influence of the first and second moments of a pulse introduced at the inlet of a column was neglected because the pulse size was extremely small.

Experimental Studies

Apparatus

A high-performance liquid chromatograph system (LC-6A, Shimadzu) was employed. A pulse of sample solutions was introduced to a fluid flow by use of a sample injector. A column was kept at a constant temperature in a thermostated water bath. The concentration of a sample in effluent was monitored by a ultraviolet detector. Detecting conditions, such as wavelength, sensitivity and light-path lengths, were chosen according to the concentration of the sample in effluent.

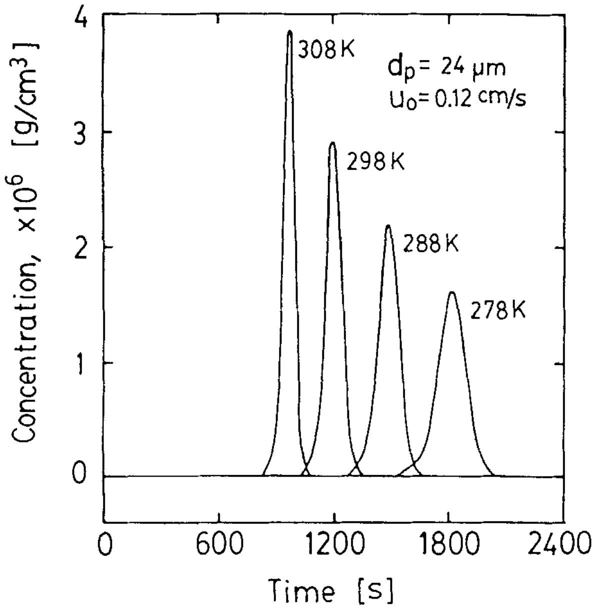

Figure 1. Examples of chromatographic peaks of PTOP at zero surface coverage (column II).

Table 1. Properties of ODS Columns and Experimental Conditions

Column	I	II	III	IV	V
Avg. particle dia., d_p [μm]	10	24	38	43	45
Particle density, ρ_p [g/cm^3]	0.85	0.87	0.90	0.90	0.86
True density [g/cm^3]	1.75	1.52	1.60	1.70	1.62
Porosity, ϵ_p	0.51	0.43	0.44	0.47	0.47
Carbon content [wt. %]	16.8	17.7	16.3	15.1	17.1
Mass of adsorbent [g]	2.25	2.27	2.17	2.16	2.20
Column size [mm]	6 ID × 150				
Void fraction, ϵ	0.38	0.38	0.43	0.44	0.43
Column temperature [K]	298	278 ~ 308	298	298	288 ~ 308
Mobile phase	Methanol/water: 70/30 (vol.)				
Superficial velocity, u_0 [cm/s]	0.05 ~ 0.12				
Sample	*p*-tert-octylphenol (PTOP, MW 206) uracil (MW 112)				

Columns and reagents

The properties of ODS columns (YMC) are shown in Table 1. Five spherical packing materials of different particle diameters were employed. The columns were 6 mm in inside diameter and 150 mm in length. The eluant was prepared by mixing methanol and pure water (70/30) volumetrically. PTOP and uracil (Tokyo-kasei) were employed as samples. Uracil is nonadsorbable on ODS.

Procedure

Experimental conditions are shown in Table 1. First, adsorption isotherms of PTOP were determined by the breakthrough experiments in the temperature range 288-308 K. Secondly, the effect of particle size and surface coverage of PTOP on axial dispersion and pore diffusion were examined by the chromatographic method. Pulse-response experiments of uracil were carried out by using PTOP solutions ranging in concentration from 0 to 1×10^{-2} g/cm^3 as eluant at 298 K. The volumetric flow rate of the eluant was varied in 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. The first and second moments were determined from the elution peaks by the moment analysis. Porosity of ODS particle was calculated from the first moment. The plot of H vs. $1/u_0$ gave the axial dispersion coefficient and tortuosity factor.

Finally runs were made for PTOP with varying surface coverage in the same manner. The column temperature was changed in the range from 278 to 308 K. The data of PTOP provided effective intraparticle diffusion coefficient. Surface diffusion coefficients at different temperatures were calculated by correcting the contribution of pore diffusion. Pore diffusivity was calculated from molecular diffusivity and tortuosity factor determined previously in the experiment for uracil.

In this study, surface coverages of PTOP were adjusted by changing concentrations of PTOP in the carrier solvent, and small concentration perturbation pulses were introduced into the carrier flow including PTOP. Each sample solution was prepared by adding a small amount of PTOP into each cor-

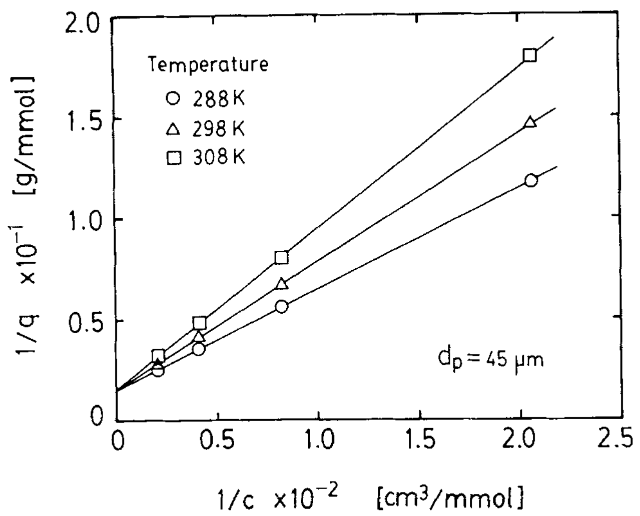

Figure 2. Langmuir plot of liquid-phase adsorption of PTOP on ODS (column V).

responding carrier solvent. The difference in PTOP concentration between the carrier solvent and the sample solution was very small. Moreover, the PTOP concentration of the pulse injected decreased with band-broading. As shown in Figure 1, chromatographic peak height was of the order of 10^{-6} g/cm^3, which was extremely small compared with the concentration range of PTOP in the carrier solvent ($0-1\times10^{-2}$ g/cm^3). The authors assumed that the change in PTOP concentration during each chromatographic measurement was negligibly small and that experimental data could be analyzed based on linear adsorption assumption. The pulse response experiments of uracil were also made in the same manner.

Results and Discussion

Adsorption equilibrium

Figure 2 shows adsorption isotherms determined by the breakthrough experiment at different temperatures. Straight lines through the same intercept were observed. The results suggest that the adsorption equilibrium relation of ODS can be expressed by the Langmuir equation. Adsorption capacity calculated from the intercept was 0.67 mmol/g and independent of temperature. As shown in Table 1, the carbon content of ODS in column V was about 17.1%, which was equivalent to 21.8% as the octadecyl bonded ligand. As the quantity of the bonded ligand on ODS is 0.7 mmol/g, which is calculated from the carbon content of ODS and the molecular weight of the ligand, one molecule of PTOP is supposed to adsorb on one octadecyl ligand. In this study, surface coverage was increased up to about 60% of the saturated amount adsorbed.

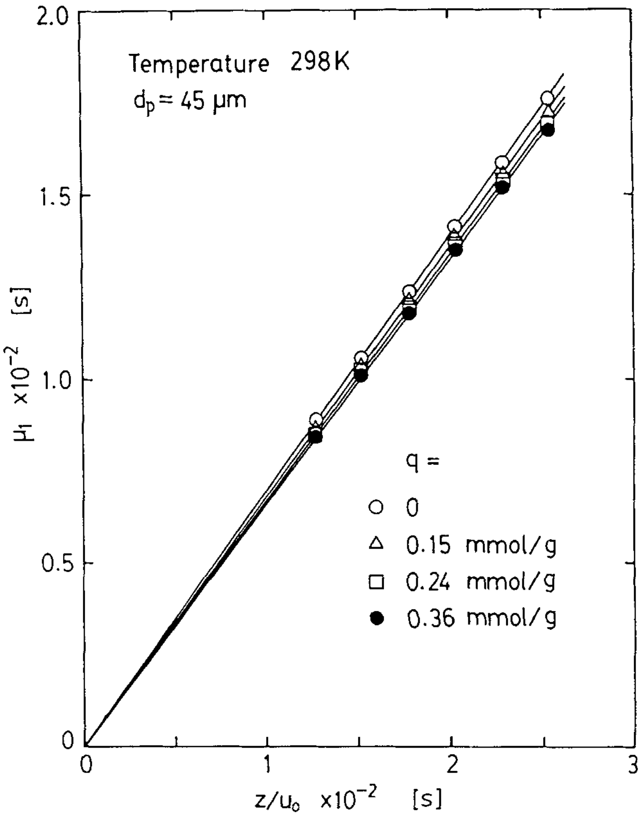

Figure 3. First moment plots of uracil at various surface coverages (column V).

Surface coverages of PTOP were adjusted by changing concentrations of PTOP in the mobile phase.

Pulse response experiment for uracil

When the eluant is methanol/water mixture 70% (v/v), uracil does not adsorb on ODS. The void volume of ODS columns was calculated from the first moment analysis of the elution peak of uracil. Figure 3 shows the plots of μ_1 vs. z/u_0 at various surface coverages. Straight lines through the origin were observed. The void volume of column V calculated from the slope of the plots is listed in Table 2. The void volume decreases linearly as the amount of PTOP adsorbed on ODS increases. The decrease in the void volume seems to be due to the decrease in the porosity of ODS particles, because most of PTOP molecules should be adsorbed on the pore wall in ODS, not on

Table 2. Properties of Axial Dispersion and Pore Diffusion in ODS

Column	q[mmol/g]	V_0[cm^3]	ϵ_p	Ez/u_0[cm]	Pe	Dp[cm^2/s]	ϵ_p/k^2	k^2
I	0	2.95	0.51	1.2×10^{-3}	0.83	8.2×10^{-7}	0.106	4.8
II	0	2.77	0.43	2.8×10^{-3}	0.85	6.9×10^{-7}	0.089	4.9
III	0	2.88	0.44	5.0×10^{-3}	0.76	6.0×10^{-7}	0.078	5.6
IV	0	2.97	0.47	5.2×10^{-3}	0.83	5.2×10^{-7}	0.067	7.0
V	0	2.95	0.47	4.0×10^{-3}	1.12	7.8×10^{-7}	0.102	4.6
	0.15	2.89	0.45	4.5×10^{-3}	1.01	7.0×10^{-7}	0.090	5.0
	0.24	2.84	0.43	4.0×10^{-3}	1.14	5.9×10^{-7}	0.077	5.6
	0.36	2.81	0.41	4.3×10^{-3}	1.06	5.5×10^{-7}	0.072	5.8

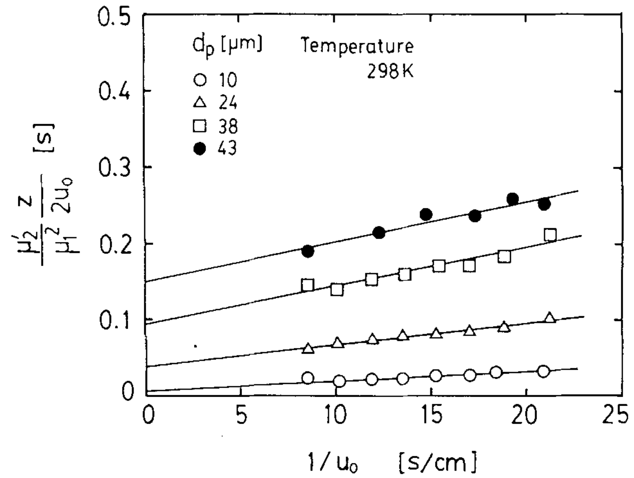

Figure 4. Second moment plots of uracil at zero surface coverage (columns I-IV).

the external surface. Table 2 shows the porosity estimated by assuming a constant void fraction of column V. Molecular volume of PTOP calculated from the decrease in the void volume is about 180 cm^3/mol, which is relatively small in comparison with the molecular weight of PTOP, 206. Part of the PTOP molecule seems to penetrate into the space between octadecyl ligands, into which a uracil molecule cannot penetrate.

The axial dispersion coefficient is considered to consist of two terms: One for molecular diffusion and the other for fluid dispersion. As the contribution of molecular diffusion is assumed to be negligibly small in liquid-phase adsorption, axial dispersion coefficient is expressed as:

$$Ez = u_0 d_p / Pe \tag{16}$$

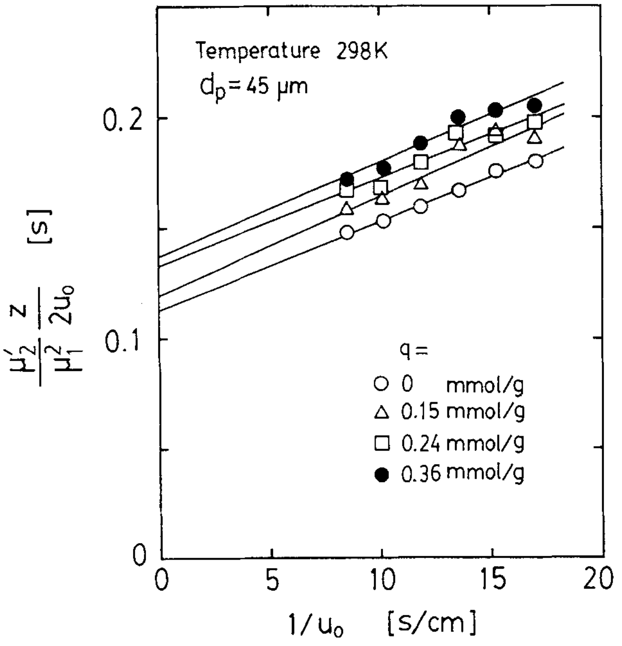

Figure 5. Second moment plots of uracil at various surface coverages (column V).

Surface coverages of PTOP were adjusted by changing concentrations of PTOP in the mobile phase.

In such a condition, a linear relation between H and $1/u_0$ is derived from Eq. 9. In Figure 4, H was plotted against $1/u_0$ for each column at zero surface coverage. Similarly, Figure 5 shows the plot of H vs. $1/u_0$ for column V at various surface coverages of PTOP. The values of Ez/u_0 and pore diffusivity determined from the slope and the intercept of the plot, respectively, are listed in Table 2. The value of Ez/u_0 was almost proportional to the particle size and scattered around the straight line representing $Pe = 0.87$.

The amount adsorbed does not affect the value of Ez/u_0, whereas the tortuosity factor changed with an increase in the amount adsorbed. The tortuosity factor was calculated from the pore diffusivity in Table 2 by:

$$Dp = (\epsilon_p / k^2) Dm \tag{17}$$

The resulting values for ODS in Table 2 are in the usual range of the tortuosity factor from 2 to 6. The tortuosity factor increased with the decrease in the porosity of ODS particles which resulted from the increase in the amount of PTOP adsorbed. The change in tortuosity factor is consistent with the result of the diffusivity in porous particles (Suzuki, 1990).

Pulse response experiment for PTOP

Figure 6 shows the plot of $(\mu_1 - t_0)/(1-\epsilon)$ vs. z/u_0 for various ODS columns at zero surface coverage. Straight lines of different slopes through the origin were observed.

Figure 7 shows the plot of $(\mu_1 - t_0)/(1-\epsilon)$ vs. z/u_0 for column V at various surface coverages of PTOP in the temperature range 288-308 K. Straight lines of different slopes through the origin were observed. The slope decreased with an increase in the concentration of PTOP in the mobile phase at each tem-

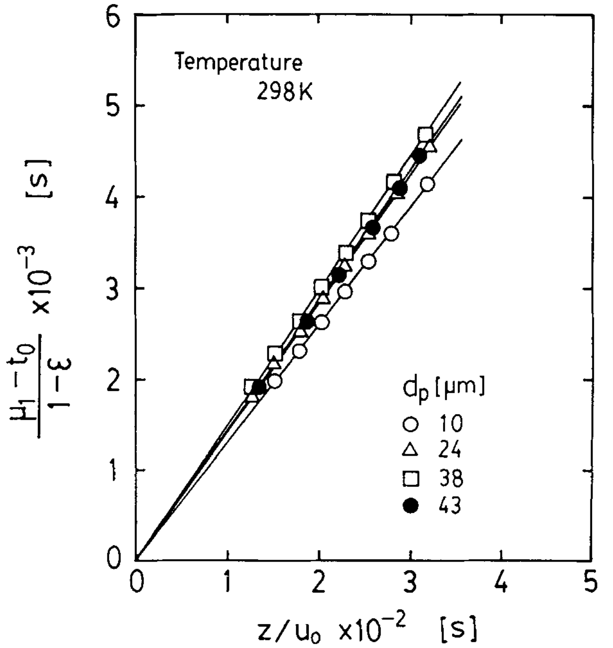

Figure 6. First moment plots of PTOP at zero surface coverage (columns I-IV).

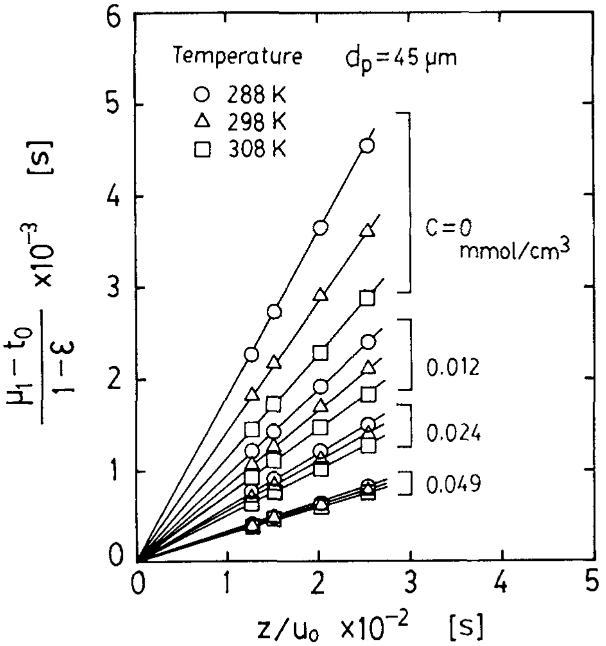

Figure 7. First moment plots of PTOP at various surface coverages (column V).

Surface coverages of PTOP were adjusted by changing concentrations of PTOP in the mobile phase.

perature. Apparent equilibrium constants, K_P, calculated from the slopes are summarized in Table 3. They are compared with the slope of the tangent to the adsorption isotherm, K_I, in Figure 2, which was determined by separate equilibrium experiments at each PTOP concentration. The values of K_P and K_I agreed with each other within about 5% error at each temperature. The agreement suggests that pulse response experiments were carried out under linear isotherm conditions.

Isosteric heat of adsorption, Q_{st}, was obtained from isotherms at different temperatures by using the Clausius-Clapeyron equation. For the Henry isotherm, Q_{st} is related to the adsorption equilibrium constant, K, by Eq. 18. Q_{st} for zero surface coverage, $Q_{st,0}$, was determined by the van't Hoff equation.

$$d \ln K/d(1/T) = -Q_{st,0}/R_g \tag{18}$$

According to Eq. 18, K was plotted against $1/T$ in Figure 8. The experimental data measured by the use of column II was also shown in Figure 8. Isosteric heat of adsorption for various amounts adsorbed, $Q_{st,a}$, was calculated from Eq. 19 by using the isosters corresponding to each amount adsorbed:

Table 3. Adsorption Equilibrium Constants [cm³/g]

	288 K		298 K		308 K	
C[mmol/cm³]	K_P	K_I	K_P	K_I	K_P	K_I
0	20.8	19.9	16.5	15.7	13.2	12.6
4.9×10^{-3}	15.8	15.3	13.1	12.7	10.8	10.5
1.2×10^{-2}	11.0	10.8	9.6	9.5	8.4	8.3
2.4×10^{-2}	6.9	6.7	6.4	6.4	5.8	5.9
4.9×10^{-2}	3.8	3.3	3.7	3.4	3.5	3.4

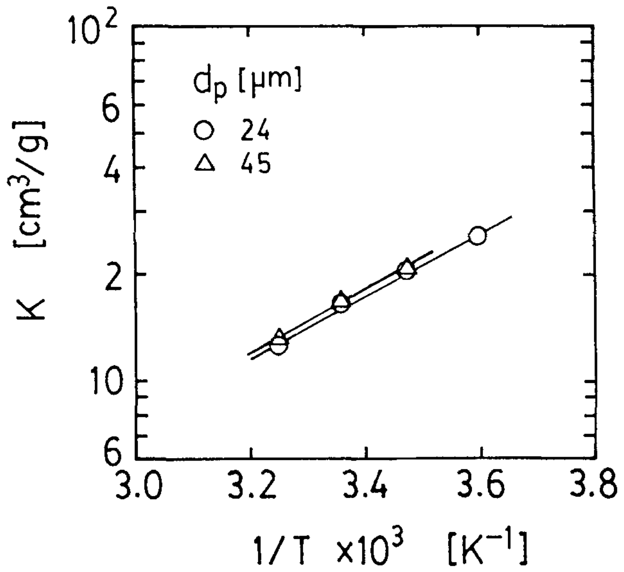

Figure 8. van't Hoff's plot of adsorption equilibrium constants of PTOP for determining isosteric heat of adsorption at zero surface coverage (columns II and V).

$$d \ln c/d(1/T) = Q_{st,a}/R_g \tag{19}$$

Concentration in equilibrium with the amount adsorbed was estimated from Figure 2 at each temperature. Isosters for various amounts adsorbed are shown in Figure 9. Resulting values of Q_{st} are listed in Table 4. Isosteric heat of adsorption is about 16 to 18 kJ/mol regardless of the amount adsorbed and particle size. The constant value of Q_{st} suggests that ODS has an energetically homogeneous surface. The value agrees with conventional results ranging from 14 to 25 kJ/mol for the liquid-phase adsorption of several organics on ODS (Knox and Vasvari, 1973; Horvath and Melander, 1977; Colin and Guiochon, 1978; Unger, 1979; Issaq and Jaroniec, 1989).

Figure 10 shows the plot of H vs. $1/u_0$ for each column at zero surface coverage. As shown in Eq. 10, the intercept of the plot gives δ_d, which depends strongly on particle size. A linear relationship through the origin was observed between H_0 and R^2. The values of surface diffusion coefficient, Ds, calculated from the intercepts in Figure 10 are listed in Table 5. The surface diffusion coefficient of PTOP in ODS is of the order of 10^{-7} to 10^{-6} cm²/s. The contribution of surface diffusion to intraparticle diffusion was compared with that of pore diffusion. Pore diffusivity, Dp, of PTOP in ODS was estimated from Eq. 17 by the use of the values of ϵ_p/k^2 in Table 2 and the molecular diffusivity, Dm, of PTOP estimated by the Wilke-Chiang equation. The contribution of surface diffusion is about 10 to 20 times greater than that of pore diffusion. It is concluded that surface diffusion is dominant for the intraparticle diffusion in ODS.

Concentration dependence of the surface diffusion coefficient in ODS was studied. Figure 11 shows the plots of H vs. $1/u_0$ under the condition that the concentration of PTOP in the mobile phase is maximum in this study. The surface diffusion coefficient at different surface coverages were determined in the same way. Figure 12 shows the dependence of Ds on the amount adsorbed, q, which is calculated from the

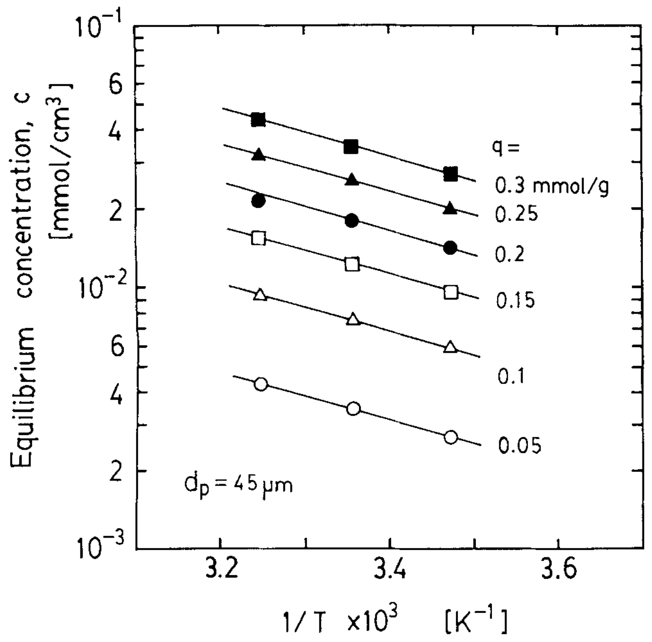

Figure 9. Clausius-Clapeyron plots of adsorption isosters of PTOP for determining isosteric heat of adsorption at various levels of amount adsorbed (column V).

Table 4. Isosteric Heat of Adsorption and Activation Energy of Surface Diffusion

Column	q_0[mmol/g]	Qst[kJ/mol]	Es[kJ/mol]
II	0	16.2	30.1
V	0	16.9	27.6
	0.05	17.3	26.6
	0.1	17.4	25.8
	0.15	17.4	25.3
	0.2	17.5	25.1
	0.25	17.6	25.2
	0.3	17.8	25.4

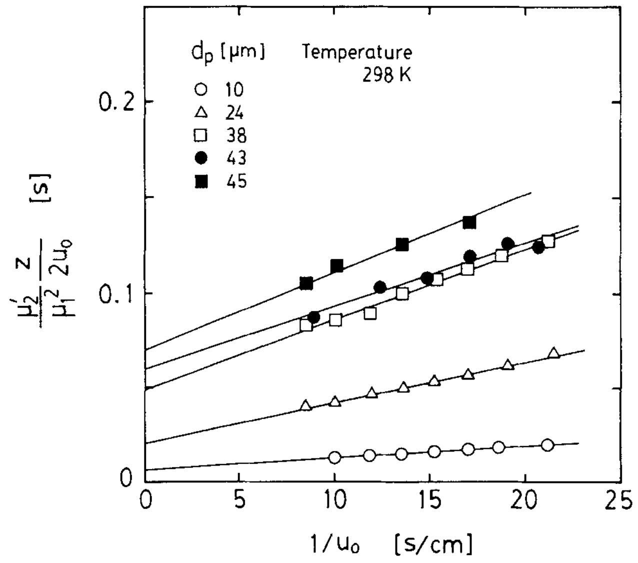

Figure 10. Second moment plots of PTOP at zero surface coverage (columns I-V).

adsorption isotherm in Figure 2. The value of Ds increased by a factor of about 2 to 3 with the increase in the amount adsorbed.

On the basis of the assumption that surface diffusion in ODS is an activated diffusion, surface diffusion coefficients at various amounts adsorbed are plotted against $1/T$ according to the Arrhenius equation in Figure 13.

$$d \ln Ds/d(1/T) = -Es/R_g \tag{20}$$

Activation energy of surface diffusion determined from Eq. 20 is also given in Table 4. The value of Es is of the order of 25 to 30 kJ/mol. The constant values of the activation energy during adsorption are consistent with the results that the isosteric heat of adsorption is unchanged regardless of the amount adsorbed and that adsorption equilibrium can be represented by the Langmuir equation. From these results it is concluded that the surface of ODS is energetically homogeneous.

The entropy change of the surface diffusion process is a very interesting subject for analyzing diffusion mechanism. It seems to be difficult, however, to accurately determine the activation entropy to quantitatively discuss the correlation between the entropy change and surface coverages. In this study, the change in entropy with an increase in the amount adsorbed was not observed.

The activation energy of surface diffusion is larger than the isosteric heat of adsorption, whereas in most cases the ratio of Es to Q_{st} has been found to range from 0.5 to 0.9 in gas-phase adsorption (Chihara et al., 1978). The difference seems to stem from the solvent effect. The solvophobic theory was

Table 5. Surface Diffusion Coefficient and Pore Diffusivity of PTOP in ODS

Column	Temp. [K]	De [cm²/s]	Dp [cm²/s]	$\rho_p KDs$ [cm²/s]	Ds [cm²/s]
I	298	3.7×10^{-6}	4.5×10^{-7}	3.3×10^{-6} (88.1%)	2.5×10^{-7}
II	278	4.3×10^{-6}	2.0×10^{-7}	4.1×10^{-6} (95.3%)	1.8×10^{-7}
	288	5.5×10^{-6}	2.8×10^{-7}	5.3×10^{-6} (95.0%)	3.0×10^{-7}
	298	6.9×10^{-6}	3.8×10^{-7}	6.5×10^{-6} (94.5%)	4.6×10^{-7}
	308	7.9×10^{-6}	5.0×10^{-7}	7.4×10^{-6} (93.7%)	6.6×10^{-7}
III	298	7.9×10^{-6}	3.3×10^{-7}	7.6×10^{-6} (95.8%)	5.1×10^{-7}
IV	298	8.2×10^{-6}	2.8×10^{-7}	7.9×10^{-6} (96.5%)	5.5×10^{-7}
V	288	6.3×10^{-6}	3.2×10^{-7}	5.9×10^{-6} (94.9%)	3.3×10^{-7}
	298	7.6×10^{-6}	4.3×10^{-7}	7.2×10^{-6} (94.4%)	5.1×10^{-7}
	308	8.5×10^{-6}	5.6×10^{-7}	8.0×10^{-6} (93.4%)	7.0×10^{-7}

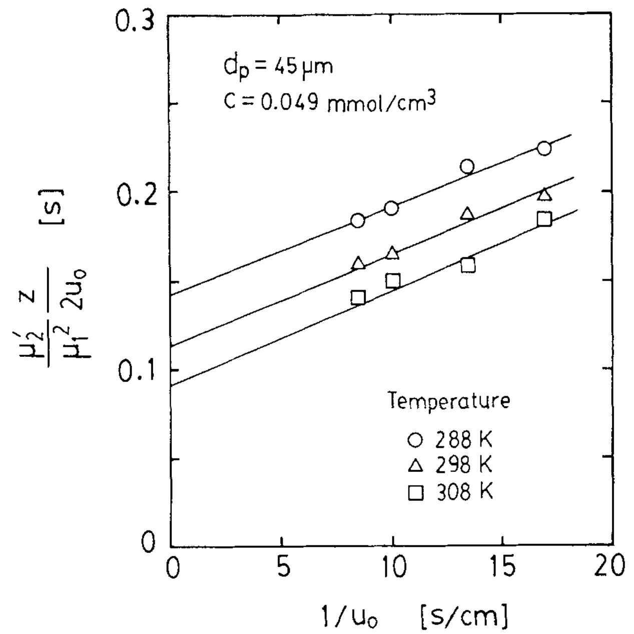

Figure 11. Second moment plots of PTOP at the highest surface coverage (column V).

Surface coverage was about 60% of the saturated amount adsorbed.

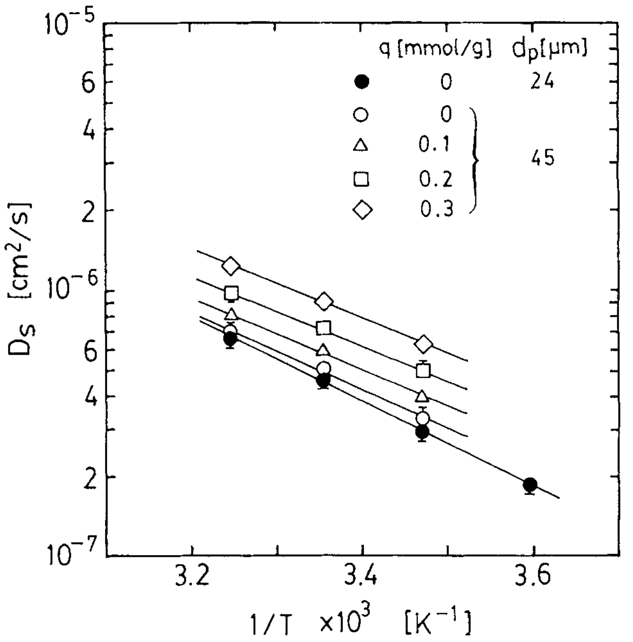

Figure 13. Temperature dependence of surface diffusion coefficients at various levels of amount adsorbed (columns II and V).

examined to explain thermodynamics of liquid-phase adsorption of PTOP on ODS. The solvophobic theory reported by Sinanoglu (1967, 1968) has been adapted to several liquid-phase adsorption systems. Belfort et al. (1984) studied the adsorbability of organic compounds onto activated carbon from dilute aqueous solutions by use of the solvophobic theory. Horvath et al. (1976) interpreted hydrophobic interaction between a solute and nonpolar stationary phase in the reversed-phase liquid chromatography.

The adsorption of PTOP onto octadecyl ligand is expressed by:

$$S + L \rightleftharpoons SL \tag{21}$$

where S is the solute, PTOP, L is the octadecyl ligand, and SL is the complex resulted from the association reaction. The solvophobic theory deals with the association reaction in solution by considering two conceptual processes. One is the hypothetical gas-phase association without the effect of the solvent. The other is the solvation of all species. The solvation process is considered to consist of two steps: the formation of a cavity in the solvent and the interaction of the species placed in the cavity with the surrounding solvent. The interaction term is assumed to be the sum of contributions of van der Waals and electrostatic.

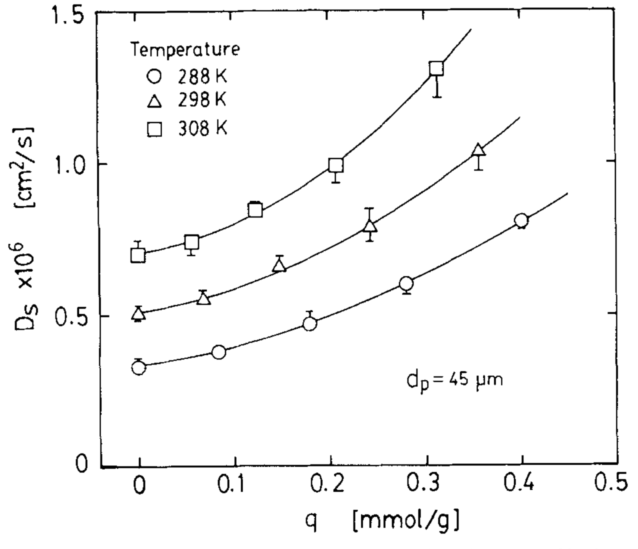

Figure 12. Dependence of surface diffusion coefficient of PTOP on the amount of PTOP adsorbed (column V).

The enthalpy change for liquid-phase adsorption was analyzed by Horvath et al. (1976):

$$\begin{aligned} -Q_{st,0} = {} & -Q_{st,\mathrm{gas}} + Q_{vdw,S} \\ & - N(\lambda-1)DP\mu_S^2(1 - d\ln\gamma/d\ln T - a_sT)/2\lambda\nu_S \\ & + N\Delta A\gamma(1 - d\ln\gamma/d\ln T - 2a_sT/3) \\ & + NA_S\gamma(\kappa^e-1)V^{2/3}[1 - d\ln\gamma/d\ln T - 2a_ST/3 \\ & - d\ln(\kappa^e-1)/d\ln T]/V_S^{2/3} - R_gT(1-aT) \end{aligned} \tag{22}$$

The value of acentric factor was estimated from that of a corresponding nonpolar homologue (Halicioglu and Sinanoglu, 1969; Horvath et al., 1976). The value of κ^e reported for methanol-water eluent systems of different composition (Horvath et al., 1976) was employed. The ratio of the molecular volume of the complex to that of the solute, λ, was estimated to be 2.5. The decrease in the surface area, ΔA, resulted from the association of the solute and octadecyl ligand is assumed to be proportional to the molecular surface area of the solute. Belfort et al. (1984) estimated ΔA as 20–30% of the solute total cavity surface area (TSA). Horvath et al. (1976) reported that ΔA was found to be about 35% of a hydrocarbonaceous surface area (HSA) for the reversed-phase liquid chromatographic separation of several organics. In this work, the value of 35% was used. The total surface area of the solute was calculated by summing the surface area increment of each group (Bondi, 1964).

The contributions of each term in Eq. 22 estimated at 298 K were −273.7 kJ/mol, 0.2 kJ/mol, and 95.6 kJ/mol for van der Waals interaction, electrostatic interaction, and cavity formation, respectively. The value of the last term in the right-hand side of Eq. 22 was calculated as 2.1 kJ/mol. In gas-phase adsorption, the ratio of the heat of adsorption to the heat of vaporization of an adsorbate was found to range from 1.2 to 1.6 (Chihara et al., 1978). The heat of vaporization of PTOP was calculated to be 55.3 kJ/mol (Reid et al., 1977). When 1.6 is taken as the ratio, the heat of adsorption in gas phase, $-Q_{st,gas}$, becomes 88.5 kJ/mol and then the isosteric heat of adsorption in solution, $-Q_{st,0}$, is calculated as −91.8 kJ/mol. The negative value of the isosteric heat of adsorption is unreasonable, because adsorption is accompanied by evolution of heat. However, it seems to be interpreted that the isosteric heat of adsorption in the liquid system is smaller than that in gas-phase adsorption, and the difference is attributed to the solvent effect, namely, the free energy change for the solvation of the solute, ligand and complex. To study thermodynamics in liquid-phase adsorption quantitatively by the solvophobic theory, appropriate values must be determined for several parameters of the theory. This is the subject that is under investigation.

An attempt was made to explain the concentration dependence of the surface diffusion coefficient by chemical potential driving force model (Ash and Barrer, 1967). Surface diffusion coefficient was expressed by:

$$Ds = Ds_0 (d \ln c / d \ln q) \tag{23}$$

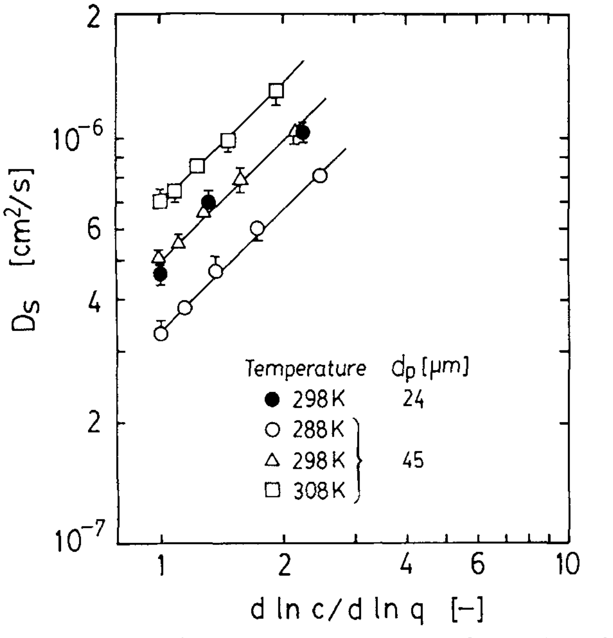

Figure 14. Plots of *Ds* vs. (*d* ln *c/d* ln *q*) (columns II and V).

The value of ($d \ln c / d \ln q$) was calculated from the adsorption isotherm in Figure 2 determined by the separate equilibrium experiment. The surface diffusion coefficient was plotted against ($d \ln c / d \ln q$) for each condition in Figure 14. Linear relations are observed between Ds and ($d \ln c / d \ln q$). This suggests that the gradient of chemical potential, rather than the concentration gradient, should be regarded as the driving force of the surface diffusion on ODS.

Conclusion

Chromatographic study was made for the liquid-phase adsorption of PTOP on ODS for various surface coverages in the temperature range 278 to 308 K. Similar measurements were made for the nonadsorbable substance, uracil.

Adsorption isotherms of PTOP were determined by the breakthrough experiment, which could be represented by the Langmuir equation. From the pulse experiments of uracil, the Peclet number of ODS columns was found to be about 0.9 and tortuosity factor was about 5. With the increase in the amount of PTOP absorbed, porosity of ODS particles decreased and tortuosity factor of pores increased. The Peclet number of the ODS column remained constant regardless of the amount adsorbed.

The first and second moments of chromatographic data of PTOP were analyzed. The surface diffusion coefficient was of the order of 10^{-7} to 10^{-6} cm²/s. Surface diffusion was dominant for the intraparticle diffusion in ODS. Isosteric heat of adsorption was found to be about 17 kJ/mol and activation energy of surface diffusion about from 25 to 30 kJ/mol. Both values were constant regardless of the amount adsorbed. It is concluded that ODS has an energetically homogeneous surface. The effect of solvent on the isosteric heat of adsorption in the liquid-phase system was discussed qualitatively by the solvophobic theory. Positive concentration dependence of the surface diffusion coefficient on the amount adsorbed was observed, and it was interpreted in terms of diffusion by potential chemical driving force.

Notation

A = surface area, cm²
a_i = coefficient of thermal expansion, K^{-1}
a_2 = association coefficient of solvent
c = concentration in mobile phase, mmol/cm³
D = $2(\epsilon' - 1)/(2\epsilon' + 1)$
De = effective intraparticle diffusion coefficient, cm²/s
Dm = molecular diffusivity, cm²/s
Dp = pore diffusivity, cm²/s
d_p = particle diameter, μm
Ds = surface diffusion coefficient, cm²/s
Es = activation energy of surface diffusion, kJ/mol
Ez = axial dispersion coefficient, cm²/s
G = Gibbs free energy, kJ/mol
H = defined by Eq. 9
H_0 = defined by Eq. 10
K = adsorption equilibrium constant, cm³/g
k_f = external mass transfer coefficient, cm/s
k^2 = tortuosity factor
M_2 = molecular weight of solvent, g/mol
N = Avogadro's number
P = $[4\pi\epsilon_0(1 - D\alpha/\nu)]^{-1}$
Pe = Peclet number
P_0 = pressure, Pa
q = amount adsorbed, mmol/g
Q_{st} = isosteric heat of adsorption, kJ/mol

R = particle radius, cm
Re_p = Reynolds number
R_g = gas constant
Sc = Schmidt number
Sh = Sherwood number
t = time, s
T = temperature, K
t_0 = defined by Eq. 8
u_0 = superficial velocity, cm/s
v = volumetric flow rate, cm^3/s
V = molar volume, cm^3/mol
Ve = volume of pipes, cm^3
V_1 = molecular volume of solute at boiling point, cm^3/mol
w = peak width at half height, s
z = longitudinal position in bed, cm

Greek letters

α = polarizability, cm^3
γ = surface tension, dyn/cm
δ_0 = defined by Eq. 3
$\delta_{ax}, \delta_f, \delta_d$ = defined by Eqs. 4-6
ϵ = void fraction in bed
ϵ' = dielectric constant of solvent
ϵ_0 = free space permittivity constant
ϵ_p = porosity
κ^e = energy correction for curved surface
λ = proportionality constant
μ = dipole moment, Debye
μ_1 = first moment, s
μ_2' = second moment, s^2
ν = molecular volume, cm^3
ρ_p = particle density, g/cm^3
η_2 = viscosity of solvent, Pa·s

Subscripts

gas = gas-phase reaction
S = solute
vdw = van der Waal's interaction

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