Adsorption Characteristics of Octadecylsilyl-Silica Gel in Gaseous Systems

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Adsorption rates and thermodynamic parameters were determined for the gas-phase adsorption of n-alkanes and benzene derivatives on octadecylsilyl-silica gel (ODS) by chromatographic measurement and moment analysis. Thermodynamic characteristics of adsorption phenomena on ODS were similar to those on the surface. The contribution of intraparticle diffusion to mass-transport resistance was dominant in the ODS column, and the role of surface diffusion was significant for the intraparticle diffusion. The values of the surface diffusion coefficient were of the order of 10^{-5} cm^2/s and could be estimated by assuming that the surface migration on ODS is a tracer diffusion of an adsorbate molecule in n-octadecane.

Introduction

High performance liquid chromatography (HPLC) has been widely employed for both analytical and preparative separations (Bidlingmeyer, 1987; Verzele, 1990; Poole and Poole, 1991). Reversed-phase mode, where octadecylsilyl-silica gel (ODS) is mainly used as a stationary phase, is extremely popular (Krstulovic and Brown, 1982; Sander and Wise, 1987; Poole and Poole, 1991). We reported earlier the study on liquid-phase adsorption of p-tert-octylphenol on the surface of ODS by the chromatographic method and the moment analysis (Miyabe and Suzuki, 1992).

Because solvents must have a significant influence on adsorption phenomena in liquid-phase adsorption, it is essential to clarify the influence of the solvents on adsorption characteristics, specifically, adsorption equilibrium, adsorption rates and thermodynamics. One approach to this subject is by comparison of experimental data in both gas- and liquid-phase adsorption systems. Of course, the experimental data should be considered quantitatively and theoretically. A detailed analysis of the data must provide information on the solvent effect in liquid-phase adsorption.

A number of studies have been made for adsorption rates and thermodynamics as well as adsorption equilibria in gaseous systems (Chihara et al., 1978a; Costa et al., 1985; Gilliland et al., 1974; Hashimoto and Smith, 1973; Kapoor et al., 1989; Kawazoe et al., 1974; Kelly and Fuller, 1980; Ruthven, 1984; Ruthven and Doetsch, 1976; Ruthven and Kumar, 1979; Schneider and Smith, 1968a,b; Shah and Ruthven, 1977; Sladek et al., 1974). It is well established that in many cases surface diffusion has an important role for intraparticle mass transport, and that the surface and/or intraparticle diffusion coefficients show positive concentration dependence on the amount adsorbed (Chihara et al., 1978b; Gilliland et al., 1974; Higashi et al., 1963; Kapoor and Yang, 1989; Kawazoe et al., 1974; Noll et al., 1992; Okazaki et al., 1981; Ruthven and Loughlin, 1971). The surface and intraparticle diffusion coefficients have been determined by several methods such as the gravimetric method (Ruthven and Loughlin, 1971), breakthrough experiment (Costa et al., 1985), steady-state technique (Gilliland et al., 1974), and the chromatographic method (Schneider and Smith, 1968b; Kawazoe et al., 1974; Chihara et al., 1978a). The chromatographic method is practically useful to determine mass-transfer rates of each process in adsorbent beds and has been applied to both gas- and liquid-phase adsorption phenomena (Suzuki, 1990). A consideration was made for the advantages and disadvantages of the chromatographic method and for the conditions, under which accurate measurements of mass-transfer rates could be achieved (Awum et al., 1988; Ramachandran and Smith, 1978; Gangwal et al., 1978). Thermodynamic properties were also studied for adsorption and diffusion on surface and in micropores in gaseous systems (Chihara et al., 1978a).

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The purpose of this article is to elucidate the adsorption characteristics of ODS in gaseous adsorption systems. Chromatographic measurements were made by using several organics as an adsorbate in the temperature range from 260 to 418 K. Pulse response curves observed experimentally were analyzed by the method of moment analysis. Mass transport rate parameters and thermodynamic properties in the gas-phase adsorption on ODS were determined from the moment analysis. Correlation of isosteric heats of adsorption with properties of the adsorbates was discussed. An attempt was also made to estimate a surface diffusion coefficient on ODS.

Moment analysis of chromatographic data

Chromatographic peaks leaving a column were analyzed by the moment method (Suzuki, 1973, 1990). The first absolute and the second central moments of the peaks are expressed as:

$$\mu_1 = \int_0^\infty Ce(t)t\,dt \Big/ \int_0^\infty Ce(t)\,dt = (z/u_0)\delta_0 \qquad (1)$$

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

where

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

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

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

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

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

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

where

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

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, was calculated from the slope of the plot.

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

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

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

The value of δ_f was calculated from Eq. 5 and its contribution to the second moment was corrected. Fluid-to-particle mass-transfer coefficient, k_f, was calculated by the equation of Carberry (1960):

$$Sh = (1.15/\epsilon^{1/2})Sc^{1/3}Re_p^{1/2} \qquad (11)$$

Molecular diffusivity of an adsorbate was estimated by the Hirschfelder equation (Reid et al., 1977):

$$Dm = 0.1883[T^3(M_1+M_2)/M_1M_2]^{1/2}/P\sigma_{12}^2\Omega_D \qquad (12)$$

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

$$De = Dp + \rho_p K Ds \qquad (13)$$

Pore diffusivity was estimated by:

$$Dp = (\epsilon_p/k^2)D_k \qquad (14)$$

The value of tortuosity factor was determined from a liquid chromatographic experiment by using uracil as an inert substance. Knudsen diffusivity was calculated by (Perry and Green, 1984):

$$D_k = (2/3)R_p(8R_gT/\pi M)^{1/2} \qquad (15)$$

Surface diffusion coefficient was determined by correcting the contribution of pore diffusion to intraparticle diffusion.

When chromatographic peak can be approximated by the normal distribution curve, the first and the second moments can be determined from the position and the width of the peak, respectively. The experimental first absolute moment includes the effect of the volume of the pipes between an injection port and a column and that between a column and a detector. The correction of the extra column volume was made as:

$$\mu_1 = \mu_{1\,\mathrm{exp}} - Ve/v \qquad (16)$$

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

$$\mu_2' = w^2/5.54 \qquad (17)$$

Experimental Studies

Apparatus

Chromatographic measurements were made by use of a conventional gas chromatograph equipped with a thermal conductivity detector (GC-9A, Shimadzu). Helium was used as a carrier gas. The flow rate of the 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 gas tight syringe. The concentration of the 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.

Table 1. Properties of ODS and Experimental Conditions

Average particle diameter, d_p (μm)	296
Particle density, ρ_p (g/cm^3)	0.95
True density (g/cm^3)	1.51
Pore volume (cm^3/g)	0.39
Porosity, ϵ_p	0.37
Pore radius (nm)	4.86
Tortuosity factor, k^2	8.4
Carbon content (wt. %)	19.8
Mass of adsorbent (g)	1.03
Column size (mm)	3.2 ID × 195
Void fraction, ϵ	0.31
Column temperature (K)	260 ~ 418
Carrier gas	He
Superficial velocity, u_0 (cm/s)	7.1 ~ 14.1

Adsorbent particle

The properties of ODS (YMC) are shown in Table 1. The average diameter of the ODS spherical in shape was determined by the scanning electron microscope. The diameters of about 200 particles were measured from micrographs and the size distribution was calculated. Pore related properties were determined by the nitrogen adsorption method. The ODS was synthesized with a monofunctional *n*-octadecyldimethylsilyl ligand. The amount of carbon, which was introduced on the surface of silica gel by chemical bonding of *n*-octadecyldimethylsilyl ligand, was 19.8 wt. %. Thermal gravity analysis (TGA) curve of ODS was measured in an atmosphere of nitrogen to elucidate thermostability of ODS. A slight decrease in weight and exothermal phenomenon were observed at a temperature of about 450 K or above. The upper limit of the experimental temperature was determined as 418 K by considering the thermolability of ODS.

ODS column

Table 1 also shows that the properties of the ODS packed column, 3.2-mm-ID and 195-mm-long column, were estimated from column volume, mass, and particle apparent density.

Gas and reagents

The purity of the carrier gas (helium) was 99.9%. Several organics such as *n*-alkanes and benzene derivatives, whose boiling point was lower than about 410 K, were employed as an adsorbate.

Procedure

Experimental conditions are also shown in Table 1. Chromatographic measurements were made with varying both column temperature and flow rate of the carrier gas. Column temperature was changed in the range from 260 to 418 K. The volumetric flow rate of the carrier gas was varied 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 introduced to the carrier gas flow at the inlet of a column. The first and the second moments of pulse-response peaks were calculated by the method of moment analysis. Adsorption equilibrium constants, axial dispersion coefficients, and intraparticle diffusion coefficients at various temperatures were determined. Surface diffusion coefficients were calculated from the intraparticle diffusion coefficients by correcting the contribution of pore diffusion. Thermodynamic parameters of gas phase adsorption on ODS were also determined.

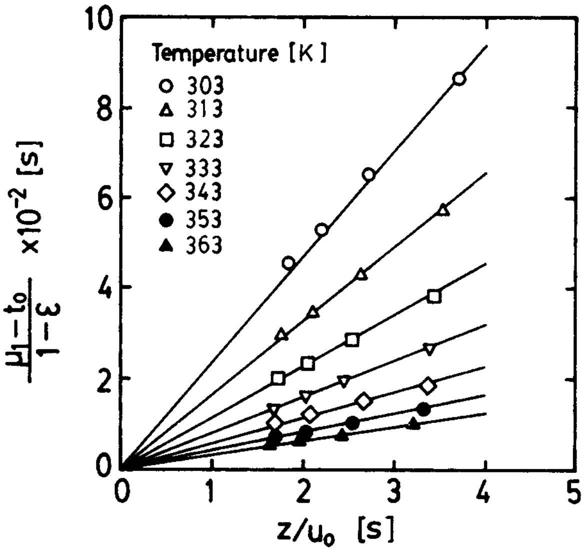

Figure 1. First moment plots of *n*-hexane at various temperatures.

Results and Discussion

Adsorption equilibrium constant

Figure 1 shows the typical plots of $(\mu_1 - t_0)/(1-\epsilon)$ vs. z/u_0 for *n*-hexane at various temperatures. Straight lines of different slopes through the origin were observed. Adsorption equilibrium constants were calculated from the slope of the first moment plots for each adsorbate at various temperatures.

The isosteric heat of adsorption, Q_{st}, was calculated by the following van't Hoff's equation:

$$K/T = (K/T)_{1/T \to 0} \exp(-Q_{st}/R_g T) \tag{18}$$

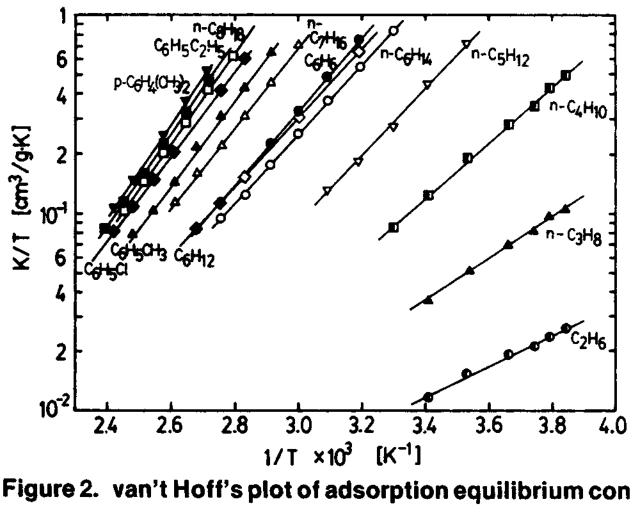

Figure 2. van't Hoff's plot of adsorption equilibrium constants.

Table 2. Experimental Results

Adsorbate	b.p. (K)	ΔHv (kJ/mol)	Qst (kJ/mol)	$(K/T)_{1/T \to 0}$ (cm^3/g·K)	Es (kJ/mol)	Ds_0 (cm^2/s)	$Qst/\Delta Hv$	Es/Qst
Ethane	184	14.7	14.7	2.9×10^{-5}	—	—	1.00	—
n-Propane	231	18.8	22.3	3.7×10^{-6}	—	—	1.19	—
n-Butane	273	21.3	26.4	2.5×10^{-6}	—	—	1.24	—
n-Pentane	309	25.8	31.7	9.8×10^{-7}	10.2	3.7×10^{-4}	1.23	0.32
n-Hexane	342	28.9	33.4	1.5×10^{-6}	14.1	1.7×10^{-3}	1.16	0.42
n-Heptane	371	31.7	38.2	7.1×10^{-7}	14.4	1.7×10^{-3}	1.21	0.38
n-Octane	398	35.0	43.4	2.9×10^{-7}	17.1	3.8×10^{-3}	1.24	0.39
cyclohexane	354	30.0	33.0	2.0×10^{-6}	15.6	2.0×10^{-3}	1.10	0.47
Benzene	353	31.7	35.3	9.6×10^{-7}	13.5	9.0×10^{-4}	1.11	0.38
Toluene	384	33.5	40.7	4.2×10^{-7}	17.5	3.6×10^{-3}	1.21	0.43
Ethylbenzene	409	33.5	43.8	2.9×10^{-7}	23.2	2.2×10^{-2}	1.31	0.53
p-Xylene	411	36.1	44.6	2.5×10^{-7}	21.1	1.2×10^{-2}	1.24	0.47
Chlorobenzene	405	37.2	40.5	6.3×10^{-7}	25.7	4.8×10^{-2}	1.09	0.63

According to Eq. 18, K/T was plotted against $1/T$ for various adsorbates in Figure 2. Resulting values of Q_{st} and $(K/T)_{1/T \to 0}$ are listed in Table 2. The values of Q_{st} were larger than those for liquid-phase adsorption (Horvath and Melander, 1977; Colin and Guiochon, 1978; Unger, 1979). The ratios of Q_{st} to the heat of vaporization of the adsorbates, ΔH_v, were ranging from 1.1 to 1.3. These values were close to the results for the adsorption of hydrocarbons on the surface of graphitized thermal carbon black (Kiselev and Poshkus, 1976). Figure 3 shows the relations between the isosteric heats of adsorption and the numbers of carbon atoms of adsorbates. Other reported results for the adsorption of hydrocarbons on other carbon base adsorbents, molecular sieving carbon 5A (Chihara et al., 1978a) and GTCB (Kiselev and Poshkus, 1976) are also included in Figure 3. A linear relation was observed for the adsorption on ODS. The values of Q_{st} of both *n*-alkanes and benzene derivatives having the same carbon number could be plotted on the same line. The tendency of the linear correlation for ODS resembled that for GTCB. The values of Q_{st} on ODS were almost equal to that on GTCB. Thermodynamic properties of the adsorption on ODS, resulting from hydrophobic interaction between an adsorbate and *n*-alkyl ligand covalently bonded on the surface of silica gel, are similar to that of adsorption phenomena on surface.

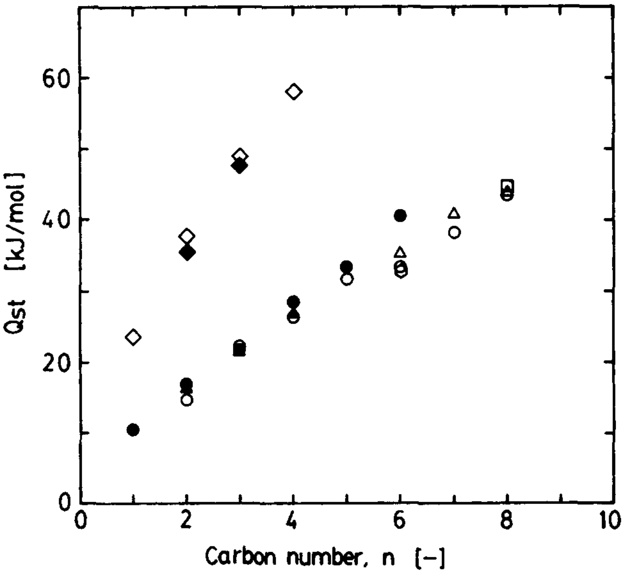

Figure 3. Correlation of isosteric heat of adsorption with the carbon number of adsorbates.

○ = *n*-alkane
△ = alkyl benzene
□ = *p*-xylene
⬡ = cyclohexane
—ODS (this work)

● = *n*-alkane
▲ = *n*-alkene
—GTCB (Kiselev and Poshkus, 1976)

◇ = *n*-alkane
◆ = *n*-alkene
—MSC5A (Chihara et al., 1978)

The logarithm of $(K/T)_{1/T \to 0}$ represents entropy change arising from the adsorption of each adsorbate. Adsorption is accompanied by the reduction of entropy in each adsorption system. The magnitude of the entropy reduction for a large molecule was larger than that for a small one.

Second moment analysis

According to Eq. 9, both the axial dispersion coefficient and the intraparticle diffusion coefficient are expected to be determined from the slope and the intercept of the plot of H vs. $1/u_0$, respectively. The axial dispersion coefficient for packed beds is considered to consist of two terms. One is for the contribution of molecular diffusion and the other is that of fluid dispersion:

$$Ez = Dm/\tau + d_p u_0/Pe \qquad (19)$$

In this study, the average diameter of ODS particles was about 0.3 mm and the values of $d_p u_0/Dm$ were larger than about 0.5 for all experiments. The contribution of fluid dispersion to the axial dispersion coefficient seemed to be dominant compared with that of molecular diffusion (Suzuki and Smith, 1971). In such a case, a linear relation between H and $1/u_0$ is expected from Eq. 9. Figure 4 shows typical plots of H vs. $1/u_0$ for *n*-hexane at different temperatures. Linear relations between H and $1/u_0$ were observed at different temperatures. The axial dispersion coefficient was determined from the slope of the plots in Figure 4. The Peclet number of the ODS column used in this study was calculated to be about 0.5. This figure is comparable to the value estimated from the empirical correlation (Suzuki and Smith, 1971):

$$Pe = 1.2 d_p \quad d_p \text{ in mm} \qquad (20)$$

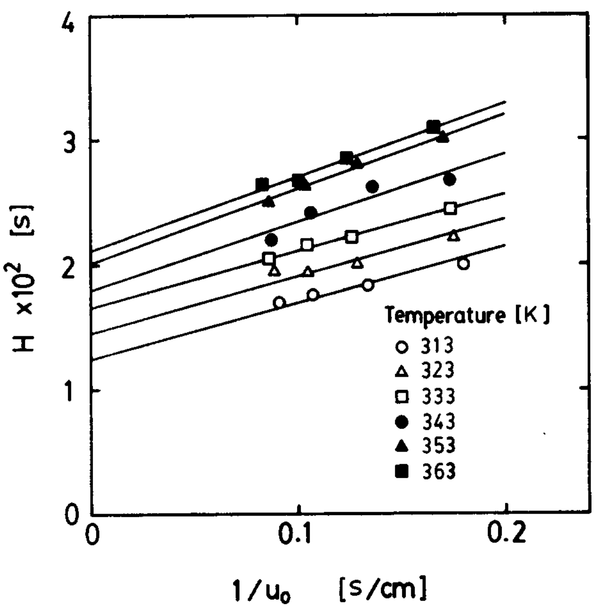

Figure 4. Second moment plots of *n*-hexane at various temperatures.

According to the result of the moment analysis of a chromatographic peak, the second moment is represented as a sum of the contributions of each transport step in a column. The contributions of each step to the second moment are compared for each adsorbate. Typical data between upper and lower temperature limits were listed in Table 3. The contribution of fluid-to-particle mass-transfer resistance was found to be about one or two orders of magnitude smaller than those of axial dispersion and intraparticle diffusion. For almost all the experiments, the contribution of axial dispersion was within 25%, and that of intraparticle diffusion was larger than 75%, suggesting that the intraparticle mass transport resistance has a significant effect in the ODS column.

The contributions of pore and surface diffusions to the intraparticle diffusion were compared with each other. As shown in Table 4, the intraparticle diffusion coefficients were a few times larger than the pore diffusivities. The contribution of the surface diffusion to global mass transport in ODS particles was found to be as much as 45–85% and changed with temperature. Surface diffusion coefficients were of the order 10^{-6}–10^{-5} cm^2/s at temperatures in the range 260–418 K. The role of the surface diffusion is significant for the intraparticle mass transport mechanism.

On the basis of the assumption that the surface diffusion in ODS was an activated diffusion, *Ds* was plotted against $1/T$ for various adsorbates according to the Arrhenius equation in Figures 5 and 6:

Table 3. Contributions of Each Rate Process to the Second Moments

Adsorbate	Temp. (K)	u_0 (cm/s)	$\mu_1/(z/u_0)$	$\mu_2'/(2z/u_0)$ (s)	δ_{ax} (%)	δ_f (%)	δ_d (%)
Benzene	323	11.8	104	239	20.2	1.7	78.1
	343	12.3	52.1	64.2	16.0	1.4	82.6
	373	12.2	21.5	13.2	17.6	1.0	81.4
Toluene	343	12.1	143	313	26.7	2.5	70.8
	363	12.9	70.1	89.6	19.7	1.8	78.4
	403	13.2	21.6	11.6	19.3	1.2	79.5
Ethylbenzene	378	12.9	82.6	106	28.6	2.2	69.2
	398	13.1	43.2	32.7	24.2	1.8	74.0
	418	13.6	24.3	13.1	23.8	1.4	74.7
p-Xylene	368	12.4	126	188	28.3	3.0	68.6
	378	12.9	94.4	122	28.2	2.5	69.3
	403	13.3	40.4	27.2	24.5	1.8	73.7
Chlorobenzene	363	12.3	102	183	25.8	2.1	72.1
	383	13.2	52.5	53.9	20.4	1.7	77.9
	413	13.3	23.4	12.2	25.1	1.3	73.6
n-Pentane	283	10.2	137	412	22.6	2.1	75.4
	293	10.8	89.0	185	19.4	1.8	78.8
	313	10.8	39.1	46.8	15.1	1.3	83.6
n-Hexane	313	11.1	116	236	24.1	2.4	73.5
	333	11.6	57.2	68.4	18.7	1.8	79.5
	363	12.0	24.3	15.7	18.4	1.3	80.2
n-Heptane	333	11.7	157	307	30.9	3.3	65.8
	353	12.0	73.0	84.7	21.6	2.4	76.0
	383	12.7	29.9	19.0	18.1	1.6	80.3
n-Octane	368	12.4	103	132	29.5	3.4	67.2
	388	12.8	53.7	44.0	25.1	2.5	72.4
	408	13.5	28.7	15.8	19.8	1.9	78.3
Cyclohexane	313	11.0	137	373	20.6	2.1	77.3
	333	11.7	69.7	111	17.4	1.7	80.9
	373	12.1	21.6	14.1	18.0	1.1	80.7

Table 4. Contributions of Pore and Surface Diffusions to Intraparticle Diffusion in ODS

Adsorbate	Temp. (K)	*De* (cm^2/s)	*Dp* (cm^2/s)	*De/Dp*	*Ds* (cm^2/s)
Benzene	323	1.3×10^{-3}	4.3×10^{-4}	3.0	5.7×10^{-6}
	343	1.1×10^{-3}	4.4×10^{-4}	2.4	8.3×10^{-6}
	373	8.1×10^{-4}	4.6×10^{-4}	1.7	1.1×10^{-5}
Toluene	343	2.0×10^{-3}	4.1×10^{-4}	5.0	7.7×10^{-6}
	363	1.4×10^{-3}	4.2×10^{-4}	3.4	9.7×10^{-6}
	403	1.0×10^{-3}	4.4×10^{-4}	2.3	2.0×10^{-5}
Ethylbenzene	378	1.9×10^{-3}	4.0×10^{-4}	4.8	1.3×10^{-5}
	398	1.6×10^{-3}	4.1×10^{-4}	3.8	1.9×10^{-5}
	418	1.3×10^{-3}	4.2×10^{-4}	3.1	2.6×10^{-5}
p-Xylene	368	2.6×10^{-3}	3.9×10^{-4}	6.5	1.2×10^{-5}
	378	2.2×10^{-3}	4.0×10^{-4}	5.5	1.4×10^{-5}
	403	1.6×10^{-3}	4.1×10^{-4}	4.0	2.1×10^{-5}
Chlorobenzene	363	1.8×10^{-3}	3.8×10^{-4}	4.8	1.0×10^{-5}
	383	1.4×10^{-3}	3.9×10^{-4}	3.7	1.4×10^{-5}
	413	1.3×10^{-3}	4.1×10^{-4}	3.1	2.6×10^{-5}
n-Pentane	283	1.3×10^{-3}	4.2×10^{-4}	3.1	4.6×10^{-6}
	293	1.1×10^{-3}	4.3×10^{-4}	2.7	5.7×10^{-6}
	313	8.3×10^{-4}	4.4×10^{-4}	1.9	7.0×10^{-6}
n-Hexane	313	1.7×10^{-3}	4.0×10^{-4}	4.2	7.7×10^{-6}
	333	1.3×10^{-3}	4.2×10^{-4}	3.0	1.0×10^{-5}
	363	9.7×10^{-4}	4.4×10^{-4}	2.2	1.6×10^{-5}
n-Heptane	333	2.6×10^{-3}	3.9×10^{-4}	6.7	9.8×10^{-6}
	353	1.7×10^{-3}	4.0×10^{-4}	4.3	1.3×10^{-5}
	383	1.2×10^{-3}	4.1×10^{-4}	2.9	1.9×10^{-5}
n-Octane	368	2.5×10^{-3}	3.8×10^{-4}	6.5	1.4×10^{-5}
	388	1.8×10^{-3}	3.9×10^{-4}	4.7	1.9×10^{-5}
	408	1.4×10^{-3}	4.0×10^{-4}	3.4	2.4×10^{-5}
Cyclohexane	313	1.4×10^{-3}	4.1×10^{-4}	3.3	4.9×10^{-6}
	333	1.1×10^{-3}	4.2×10^{-4}	2.7	7.2×10^{-6}
	373	8.4×10^{-4}	4.5×10^{-4}	1.9	1.3×10^{-5}

$$Ds = Ds_0 \exp(-Es/R_gT) \tag{21}$$

Activation energy of the surface diffusion, *Es*, and preexponential factor, Ds_0, determined from Eq. 21 are also listed in Table 2. The value of *Es* was of the order 10 to 26 kJ/mol. This figure is smaller than the corresponding isosteric heat of adsorption. The ratio of *Es* to Q_{st} was found to range from 0.4 to 0.6. It was suggested that in gaseous systems the ratio of *Es* to Q_{st} was about 0.5 for surface diffusion (Gilliland et al., 1974; Sladek et al., 1974; Chihara et al., 1978a). From these results, it is concluded that mass transport phenomenon of adsorbed molecules on ODS is similar to surface diffusion.

An attempt was made to estimate the surface diffusion coefficients. On the basis of the assumption that the surface migration on ODS could be regarded as a tracer diffusion of a solute in *n*-octadecane, the tracer diffusivity was calculated. For the prediction of tracer diffusivities in binary systems involving long-chain hydrocarbons, an empirical correlation was presented (Chen and Chen, 1985):

$$10^9\, D_{12}\eta_2/TV_{b2}^{2/3} = 11.96/V_{b1}^{1/3} - 0.8796 \tag{22}$$

Tracer diffusivities calculated according to Eq. 22 were also illustrated in Figures 5 and 6. The values estimated were somewhat larger than the experimental data but were the same order of magnitude. Resulting values estimated by the other equation (Van Geet and Adamson, 1965) were almost equal to those calculated by Eq. 22. The difference between the experimental data and the calculated values may be attributed to several factors. For instance, the influence of the tortuosity factor of the surface on the surface diffusion should be considered. Actually, the mobility of *n*-octadecylsilyl ligand seems to be restricted in comparison with a liquid-like state, because one end of the alkyl chain is chemically bonded on the surface of silica gel.

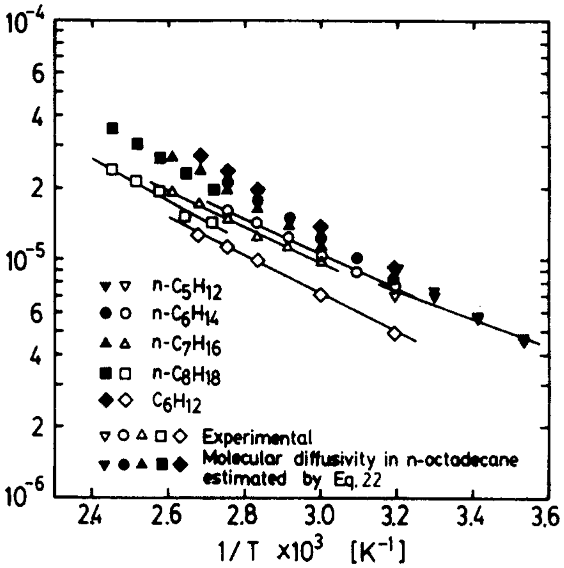

Figure 5. Arrhenius' plot of surface diffusion coefficients for saturated hydrocarbons.

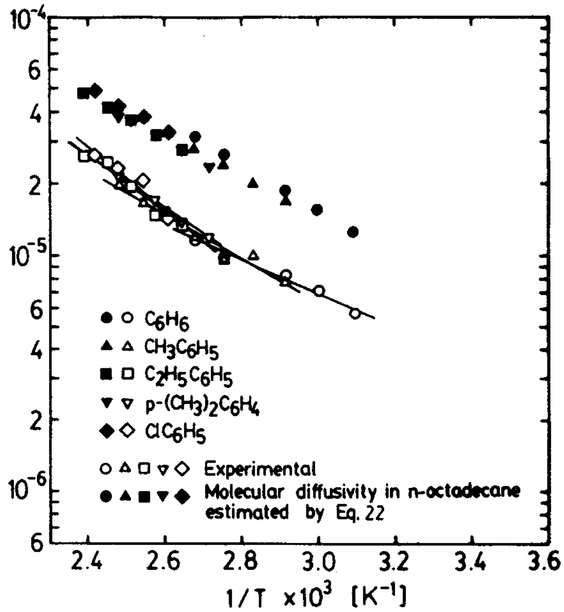

Figure 6. Arrhenius' plot of surface diffusion coefficients for benzene derivatives.

Conclusion

Chromatographic study was made for gas-phase adsorption of several organics on ODS for zero surface coverage in the temperature range 260 to 418 K.

Isosteric heats of adsorption were about 1.2 times the heats of vaporization. The ratios of the activation energy of surface diffusion to the isosteric heat of adsorption were ranging from 0.4 to 0.6. Characteristics of adsorption phenomena on ODS were similar to those of adsorption and mass transport on surface.

From analysis of second moment data it was elucidated that the contribution of intraparticle diffusion to global mass transport resistance in the ODS column was significant compared with those of other rate steps. Surface diffusion had an important role for the intraparticle diffusion. In ODS particles, about 45-85% of adsorbate molecules migrated by means of the surface diffusion.

The values of surface diffusion coefficient experimentally determined were of the order of 10^{-5} cm^2/s. Estimation of the surface diffusion coefficient was attempted on the basis of the assumption that the surface migration on ODS could be regarded as a tracer diffusion of a solute in *n*-octadecane. The values calculated were comparable to experimental data.

Notation

Ce = concentration in the effluent, g/cm^3
d_p = particle diameter, cm
D = tracer diffusivity, cm^2/s
De = intraparticle diffusion coefficient, cm^2/s
D_k = Knudsen diffusivity, cm^2/s
Dm = molecular diffusivity, cm^2/s
Dp = pore diffusion coefficient, cm^2/s
Ds = surface diffusion coefficient, cm^2/s
Ds_0 = preexponential factor for the Arrhenius plot of Ds, cm^2/s
Es = activation energy of surface diffusion, kJ/mol
Ez = axial dispersion coefficient, cm^2/s
H = defined by Eq. 9
ΔH_v = heat of vaporization, kJ/mol
H_0 = defined by Eq. 10
K = adsorption equilibrium constant, cm^3/g
k_f = external mass-transfer coefficient, cm/s
k^2 = tortuosity factor of pores
M = molecular weight, g/mol
n = carbon number
P = pressure, Pa
Pe = Peclet number
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_0 = defined by Eq. 8
T = temperature, K
u_0 = superficial velocity, cm/s
v = volumetric flow rate, cm^3/s
V_b = molar volume at normal boiling point, cm^3/mol
Ve = volume of pipes, cm^3
w = peak width at half height, s
z = longitudinal position in bed, cm

Greek letters

δ_0 = defined by Eq. 3
$\delta_{ax}, \delta_d, \delta_f$ = defined by Eqs. 4-6
ϵ = void fraction in bed
ϵ_p = porosity
η_2 = viscosity of solvent, Pa·s
μ_1 = first moment, s
μ_2' = second moment, s^2
ρ_p = particle density, g/cm^3
σ = collision diameter, cm
τ = tortuosity factor of interstitial fluid path
Ω_D = collision function

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