Solvent Effect on Adsorption Phenomena in Reversed-Phase Liquid Chromatography

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The effect of solvent and mobile-phase composition on adsorption characteristics in liquid-phase absorption is studied. Comparing experimental adsorption data for several organics in both gas- and liquid-phase systems confirms that adsorption equilibrium constant K and isosteric heat of adsorption Q_{st} are smaller than those in corresponding gaseous systems. The logarithm of K almost linearly increases as methanol composition decreases. Solvophobic theory applied quantitatively analyzes these solvent effects. Estimation methods for three parameters influence calculation results: solvent effects on K can be quantitatively analyzed; the adsorbability of adsorbates can be estimated from the value of ΔG_{solv} for each homologue in a reversed-phase liquid chromatographic system; and the solvent effect on Q_{st} cannot be satisfactorily interpreted. It is, however, confirmed that Q_{st} is influenced by a solvent and an apparent small value is observed in liquid-phase adsorption.

Introduction

In liquid chromatography where solvents are used as a mobile phase, separations can be carried out under low-temperature conditions compared with gas chromatography. Any kind of substance soluble in a solvent can be separated by liquid chromatography, properties of which arise from the presence of a solvent in a liquid chromatographic system differing considerably from those of gas chromatography. To use liquid chromatography for both analytical and preparative separations in practice, one must consider optimization of chromatographic conditions. Since adsorption phenomena are significantly influenced by a solvent in a liquid-phase system, adjustment of mobile-phase conditions plays an important role in the optimization process of liquid chromatography.

A great number of works have been reported on the effect of a solvent, particularly mobile-phase composition, on retention behaviors of reversed-phase liquid chromatography. Nearly linear relations have been experimentally observed between the logarithm of capacity factor (or adsorption equilibrium constant) and volumetric fraction of an organic solvent in mobile phase. Analysis and prediction of chromatographic separations are usually carried out based on the linear relations. Many experimental data concerning the linear relations have been reported and suggest different conclusions relating to the linearity in the range of capacity factor less than unity and the influence of the kind of solvent on the linearity (Berendsen and de Galan, 1980; Hennion et al., 1978; Karger et al., 1976; Schoenmakers et al., 1979).

Solvophobic theory provides a theoretical framework required to quantitatively explain the influence of solvent on retention behaviors of reversed-phase liquid chromatography (Horvath et al., 1976, 1977, 1978). Effect of solvent composition on retention behaviors in reversed-phase liquid chromatography has also been studied by the solvophobic theory. Horvath et al. (1976) investigated solvent effects on retention behaviors of toluic acid under reversed-phase conditions that methanol/water and acetonitrile/water mixtures were used as a mobile phase and octadecylsilyl silica gel (ODS) was employed as a stationary phase. They attempted to quantitatively explain a variation of solvent effect accompanied by a change in mobile-phase composition. Several subjects still remain to be clarified for estimation of parameters of the solvophobic theory in order to make a more detailed analysis on the solvent effects.

In reversed-phase liquid chromatography with ODS, it is

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empirically known that aliphatic saturated compounds are adsorbed in preference to branch or aromatic unsaturated ones (Poole and Poole, 1991; Sander and Wise, 1987). In order to correlate adsorbability in reversed-phase mode with properties of adsorbates, several empirical parameters such as partition coefficient between n-octanol and water and solubility parameter have been proposed. On the other hand, Belfort et al. (1984) theoretically studied liquid-phase adsorption of several organics on an activated carbon from aqueous solution. Adsorbability of the adsorbates were correlated with surface area based on the solvophobic theory. Mockel et al. (1987) also investigated the relationship between retention in reversed-phase liquid chromatography and surface area for several kinds of adsorbates.

In previous articles, we studied adsorption phenomena of several kinds of adsorbates on the surface of ODS by the chromatographic technique and the moment analysis method in gas- and liquid-phase adsorption systems (Miyabe and Suzuki, 1992, 1993a,b, 1994). Solvent effects on adsorption were experimentally confirmed in reversed-phase liquid chromatographic systems. For liquid-phase adsorption on ODS, activation energy of surface diffusion was larger than isosteric heat of adsorption. This condition suggests that it must be easier for adsorbed molecules to desorb into the bulk phase than to migrate on the surface. This apparently unreasonable situation may result from the influence of a solvent. Similar results have also been reported by several investigators for liquid-phase adsorption systems (Awum et al., 1988; Ching et al., 1989; Ma et al., 1988). Quantitative analyses of the experimental data, however, have not been carried out. Very few works have been reported on solvent effects on adsorption rates and thermodynamic parameters such as isosteric heat of adsorption and activation energy of surface diffusion in reversed-phase liquid chromatography. One approach to the subject may be a comparison between experimental results determined in both gas- and liquid-phase adsorption systems, in which the same adsorbents and adsorbates are used.

This article is concerned with the effect of solvent and solvent composition on adsorption equilibrium and thermodynamic parameters of reversed-phase liquid chromatography. The solvent effect was elucidated by comparing adsorption data experimentally measured in both gas- and liquid-phase adsorption systems. Adsorption equilibrium constant and isosteric heat of adsorption in liquid-phase adsorption were quantitatively analyzed by the solvophobic theory. The estimation method of three parameters, which extremely affect calculation results of the solvophobic theory, was studied.

Solvophobic Theory

The solvophobic theory, originally put forward by Sinanoglu (1967, 1968) and Halicioglu and Sinanoglu (1969) to explain thermodynamically chemical and physical phenomena, 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 the solvophobic theory. Horvath et al. (1976) interpreted hydrophobic interaction between a solute and nonpolar stationary phase in reversed-phase liquid chromatography.

Adsorption phenomena of an adsorbate onto octadecyl ligand is expressed by the following reaction:

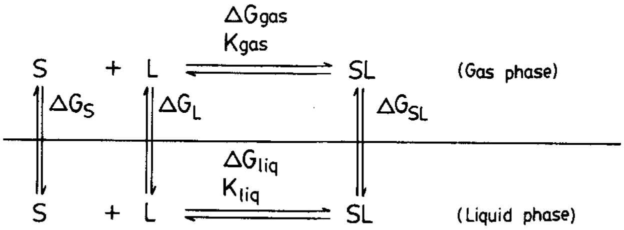

Figure 1. Interpretation of liquid-phase adsorption by the solvophobic theory.

$$\mathrm{S}+\mathrm{L} \rightleftharpoons \mathrm{SL} \tag{1}$$

where S is the adsorbate, L octadecyl ligand, and SL complex associated by the reaction. The adsorption equilibrium constant, K_{liq}, is related to the free energy change, ΔG_{liq},

$$\Delta G_{\text{liq}} = -R_g T \ln K_{\text{liq}} \tag{2}$$

The solvophobic theory deals with the association reaction in a liquid-phase system by considering two conceptual processes as shown in Figure 1. One is the hypothetical gas-phase association reaction without the effect of the solvent and the other is the solvation of all species. The solvation process is considered to consist of two steps, namely 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. The overall free energy change for the association in solution is given by:

$$\begin{aligned}\Delta G_{\text{liq}} = \Delta G_{\text{gas}} &+ (\Delta G_{\text{cav,SL}} + \Delta G_{\text{vdw,SL}} + \Delta G_{\text{es,SL}}) \\ &- (\Delta G_{\text{cav,S}} + \Delta G_{\text{vdw,S}} + \Delta G_{\text{es,S}}) \\ &- (\Delta G_{\text{cav,L}} + \Delta G_{\text{vdw,L}} + \Delta G_{\text{es,L}}) - R_g T \ln (R_g T/P_0 V)\end{aligned} \tag{3}$$

The free energy change for cavity formation is expressed as:

$$\Delta G_{\text{cav},i} = \kappa_i^e A_i \gamma (1-W) N \tag{4}$$

where

$$W_i = (1-\kappa_i^s/\kappa_i^e)[(d\ln\gamma/d\ln T) + 2a_i T/3] \tag{5}$$

$$\kappa_i^e = 1 + (\kappa^e - 1)(V/V_i)^{2/3} \tag{6}$$

The free energy change of the interaction due to the dispersion forces is calculated by the following equation (Horvath et al., 1976; Belfort et al., 1984):

$$\Delta G_{\text{vdw},i} = -0.606 \Delta_i D_i D Q \tag{7}$$

where

$$\Delta_i = 1.35 I_i I/(I_i + I) \tag{8}$$

$$D_i = (n_i^2 - 1)/(n_i^2 + 2) \tag{9}$$

$$Q = \nu_i\Big[\sigma_{\mathrm{av}}^6\{(t'^2/11)+(t'/5)+(1/9)\}/(r_{\mathrm{av}}-l_{\mathrm{av}})^9 - \{(t'^2/5)+(t'/2)+(1/3)\}/(r_{\mathrm{av}}-l_{\mathrm{av}})^3\Big] \quad (10)$$

$$t' = l_{\mathrm{av}}/(r_{\mathrm{av}}-l_{\mathrm{av}}) \quad (11)$$

$$r_{\mathrm{av}} = (r_i + r)/2 \quad (12)$$

$$l_{\mathrm{av}} = (l_i + 1)/2 \quad (13)$$

$$\sigma_{\mathrm{av}} = (\sigma_i + \sigma)/2 \quad (14)$$

$$r_i = 1.74(3\nu_i/4\pi)^{1/3} \quad (15)$$

Horvath et al. and Belfort et al. employed Eqs. 16 and 17 to estimate molecular-size parameters:

$$l_i = r_i(0.24+7\omega_i)/(3.24+7\omega_i) \quad (16)$$

$$\sigma_i = 4.64(3\nu_i/4\pi)^{1/3}(3.24+7\omega_i) \quad (17)$$

Tee et al. (1966) proposed a method based on the corresponding states correlation to estimate coefficients of the Kihara potential function. These coefficients were determined from second virial coefficient and viscosity experimentally measured. In this study, molecular-size parameters were calculated by the two methods. The value of acentric factor was estimated from that of a corresponding nonpolar homologue (Halicioglu and Sinanoglu, 1969; Horvath et al., 1976; Ried et al., 1977) and nonsubscripted variables indicate the values for the solvent. The value of D and the core-size parameters for the solvent were calculated in the same way.

The free energy change coming from the electrostatic forces is approximated by the equation:

$$\Delta G_{\mathrm{es},i} = -N\mu_i^2\Psi P/2\nu_i \quad (18)$$

where

$$\Psi = 2(\epsilon'-1)/(2\epsilon'+1) \quad (19)$$

$$P = [4\pi\epsilon_0(1-\Psi\alpha_i/\nu_i)]^{-1} \quad (20)$$

Substituting Eqs. 4–20 into Eq. 3 gives:

$$\begin{aligned}\Delta G_{\mathrm{liq}} = \Delta G_{\mathrm{gas}} &+ [\kappa_{\mathrm{SL}}^e A_{\mathrm{SL}}\gamma(1-W_{\mathrm{SL}})N + \Delta G_{\mathrm{vdw,SL}} - N\mu_{\mathrm{SL}}^2\Psi P/2\nu_{\mathrm{SL}}] \\ &- [\kappa_{\mathrm{S}}^e A_{\mathrm{S}}\gamma(1-W_s)N + \Delta G_{\mathrm{vdw,S}} - N\mu_{\mathrm{S}}^2\Psi P/2\nu_{\mathrm{S}}] \\ &- [\kappa_{\mathrm{L}}^e A_{\mathrm{L}}\gamma(1-W_{\mathrm{L}})N + \Delta G_{\mathrm{vdw,L}} - N\mu_{\mathrm{L}}^2\Psi P/2\nu_{\mathrm{L}}] \\ &- R_gT\ln(R_gT/P_0V) \quad (21)\end{aligned}$$

Several simplifications of the algebraic equations were made in the applications of the solvophobic theory (Horvath et al., 1976; Belfort et al., 1984). Since octadecyl ligand is nonpolar stationary phase, the following assumption can be made:

$$\mu_{\mathrm{L}} = 0 \quad (22)$$

$$\mu_{\mathrm{SL}} = \mu_{\mathrm{S}} \quad (23)$$

The octadecyl ligand is larger than the adsorbate molecule,

$$\Delta G_{\mathrm{vdw,SL}} = \Delta G_{\mathrm{vdw,L}} \quad (24)$$

In addition, if the size of both octadecyl ligand and the adsorbate is much larger than that of a solvent:

$$W_{\mathrm{SL}} = W_{\mathrm{S}} = W_{\mathrm{L}} = 0 \quad (25)$$

The value of κ_i^e was estimated from Eq. 6.

$$\kappa_{\mathrm{SL}}^e = \kappa_{\mathrm{L}}^e = 1 \quad (26)$$

Horvath et al. (1976) reported the value of κ^e for methanol-water eluent systems of different compositions. They estimated the values by analyzing chromatographic data measured experimentally. The value for 70 vol. % methanol was evaluated as 2.1. On the other hand, the authors estimated the corresponding value of κ^e from apparent heat of vaporization, which was calculated from the temperature dependence of viscosity of the mixed solvents. Resulting value of κ^e was 3.0.

The molecular volume of the complex is expressed by a multiple of the molecular volume of the solute:

$$\nu_{\mathrm{SL}} = \lambda\nu_s \quad (27)$$

As described later in this article, the contribution of electrostatic interaction is negligibly small in hydrophobic adsorption phenomena on ODS and λ is contained in the term. The contribution of λ to calculation results is also negligible.

The total surface area of the complex is expressed by

$$A_{\mathrm{SL}} = A_{\mathrm{S}} + A_{\mathrm{L}} - \Delta A \quad (28)$$

where ΔA is the decrease of the surface area resulting from the association of the solute and octadecyl ligand. The value of ΔA 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. Horvath et al. (1976) reported that ΔA was found to be about 35% of a hydrocarbonaceous surface area for the reversed-phase liquid chromatographic separation of several organics. In this work experimental data were analyzed in a similar manner. The total surface area of the solute was calculated by summing the surface area increment of each group (Bondi, 1964). The functional groups used in this study are listed in Table 1.

By taking the above assumptions, Eq. 21 is expressed as:

$$\begin{aligned}\Delta G_{\mathrm{liq}} = \Delta G_{\mathrm{gas}} - \Delta G_{\mathrm{vdw,S}} + N(\lambda-1)\mu_{\mathrm{S}}^2\Psi P/(2\lambda\nu_{\mathrm{S}}) - N\Delta A\gamma \\ - NA_s(\kappa^e-1)V^{2/3}\gamma/V_{\mathrm{S}}^{2/3} - R_gT\ln(R_gT/P_0V) \quad (29)\end{aligned}$$

The difference between ΔG_{liq} and ΔG_{gas} represents the solvent effect, ΔG_{solv}, on the free energy change in a liquid-phase adsorption:

$$\begin{aligned}\Delta G_{\mathrm{solv}} = \Delta G_{\mathrm{liq}} - \Delta G_{\mathrm{gas}} = -\Delta G_{\mathrm{vdw,S}} \\ + N(\lambda-1)\mu_{\mathrm{S}}^2\Psi P/(2\lambda\nu_{\mathrm{S}}) - N\Delta A\gamma \\ - NA_{\mathrm{S}}(\kappa^e-1)V^{2/3}\gamma/V_{\mathrm{S}}^{2/3} - R_gT\ln(R_gT/P_0V) \quad (30)\end{aligned}$$

Table 1. Group Contributions to the van der Waals Volume and Surface Area of Hydrocarbons (Bondi, 1964)

Groups	V_W, cm^3/mol	A_w, cm^2/mol $\times 10^9$
$-\overset{\mid}{\underset{\mid}{C}}-$	3.33	0
$-\overset{\mid}{\underset{\mid}{C}}H$	6.78	0.57
$>CH_2$	10.23	1.35
$-CH_3$	13.67	2.12
CH_4	17.12	2.90
n-Paraffins	6.88 + 10.23 Nc	1.54 + 1.35 Nc
Olefinic		
$=C=$	6.96	
$>C=C<$	10.02	0.61
$=\overset{\mid}{C}H$	8.47	1.08
$=CH_2$	11.94	1.86
$>C=CH_2$	16.95	2.17
$>C=\overset{\mid}{C}H$	13.49	1.39
Acetylenic		
$-C\equiv$	8.05	0.98
$\equiv C-H$	11.55	1.74
$\equiv C-$(in diacetylene)	7.82	
Aromatic		
$\geqslant C-$(condensation)	4.74	0.21
$\geqslant C-$(alkyl)	5.54	0.30
$\geqslant C-H$	8.06	1.00
Benzene	48.36	6.01
Phenyl	45.84	5.33
Naphthalene	73.97	8.44
Naphthyl	71.45	7.76

In this study, the experimental value of ΔG_{solv} was calculated from ΔG_{liq} and ΔG_{gas} obtained respectively in liquid-phase and gaseous adsorption systems and quantitatively analyzed according to Eq. 30. The estimating methods were also studied for the three parameters in Eq. 30, which significantly influence the analysis result, namely molecular-size parameter, reduction of hydrophobic surface area resulting from adsorption, and the value of κ^e.

Isosteric heat of adsorption was expressed as follows:

$$\begin{aligned}-\Delta Q_{\text{solv}} &= -\Delta Q_{\text{st,liq}} + \Delta Q_{\text{st,gas}} = \Delta Q_{\text{vdw,S}}\\ &\quad - N(\lambda-1)\Psi P\mu_s^2[1-(d\ln\gamma/d\ln T)-a_S T]/2\lambda\nu_s\\ &\quad + N\Delta A\gamma[1-(d\ln\gamma/d\ln T)-2a_S T/3]\\ &\quad + NA_S(\kappa^e-1)V^{2/3}[1-(d\ln\gamma/d\ln T)\\ &\quad -2a_S T/3 - d\ln(\kappa^e-1)/d\ln T]/V_s^{2/3}\\ &\quad - R_g T(1-aT) \qquad (31)\end{aligned}$$

Solvent effect on isosteric heat of adsorption in liquid phase was also analyzed quantitatively by Eq. 31.

Experimental

The properties of ODS and experimental conditions of both gas- and liquid-phase adsorption are listed in Table 2.

Table 2. Properties of ODS Column and Experimental Conditions

	Liquid	Gas
Avg. particle dia. d_p (μm)	45	296
Particle dens., ρ_p (g/cm^3)	0.86	0.95
True dens. (g/cm^3)	1.59 (100, 80), 1.60 (60), 1.63 (40, 20), 1.70 (0)	1.51
Pore vol. (cm^3/g)	0.53 (100, 80, 60), 0.55 (40, 20), 0.57 (0)	0.39
Porosity, ϵ_p(—)	0.46 (100, 80, 60), 0.47 (40, 20), 0.49 (0)	0.37
Carbon content (wt. %)	17.1	19.8
Mass of ads. (g)	2.1	1.0
Column size (mm)	6 I.D. × 150	3.2 I.D. × 195
Void fraction, ϵ	0.43	0.31
Column temp. (K)	288 ~ 308	260 ~ 418
Mobile phase	Methanol/water: 100/0 ~ 0/100 (vol.)	He
Superficial vel., u_0 (cm/s)	0.66 ~ 0.12	5 ~ 14

( ): Volumetric ratio of methanol in methanol/water mobile phase.

Pulse response experiments in gaseous systems were carried out by using gas chromatograph equipped with thermal conductivity detector (TCD). A glass column was prepared by packing ODS particles, and helium was used as a carrier gas.

Chromatographic elution peaks were measured by using a conventional high performance liquid chromatograph in liquid-phase adsorption. The size of a column was 6 mm ID and 150 mm in length, packed with spherical ODS particles. Methanol/water mixtures ranging in concentration of methanol from 0 to 100 vol. % were used as a mobile phase. Pore volume and porosity of ODS particles slightly increased in methanol fraction in mobile phase. Sodium nitrate, uracil, and methanol were used as an inert substance to determine a void volume of the ODS column.

In both gas- and liquid-phase adsorption systems, pulse response curves measured with varying superficial velocity of a carrier gas or a mobile phase and column temperature were analyzed by the method of moment (Suzuki, 1973, 1990). Owing to thermostability of ODS, saturated hydrocarbons and benzene derivatives having normal boiling point less than 423 K were employed as an adsorbate in gaseous systems. Details of pulse response experiments and moment analysis method were reported earlier (Miyabe and Suzuki, 1992).

Results and Discussion

Determination of column void volume

When retention data are analyzed quantitatively, a void volume of a column is one of the most important parameters. In practice, it is not easy to determine the void volume accurately. Many kinds of substances and methods have been proposed. One convenient method employed usually is a pulse response method in which sodium nitrate, uracil, and an organic modifier used as a component of a mobile phase (methanol in this study) are introduced, as well as a gravimetric method in which mixed solvents of different compositions are used as a mobile phase.

Wells and Clark (1981) proposed a pulse response method using sodium nitrate as an inert substance and discussed an effect of polar components on the determination of a column void volume in reversed-phase liquid chromatography. They recommended pulse response methods for determining a void

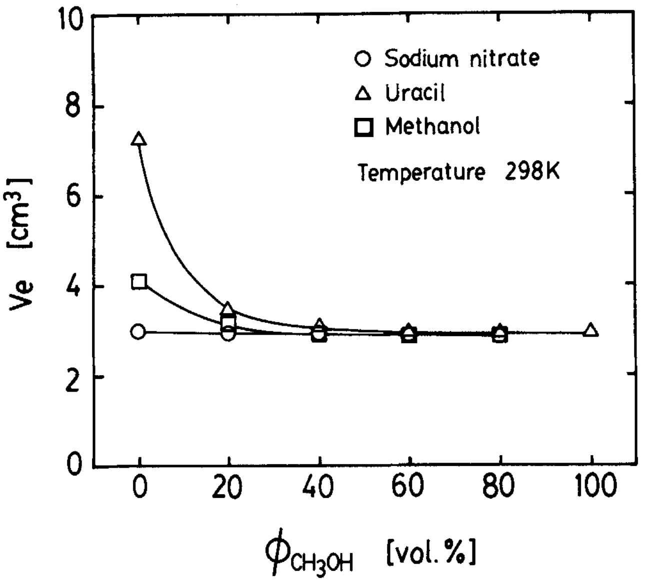

Figure 2. Correlation of the elution volume of adsorbate with methanol composition of the mobile phase.

fraction of a column by injecting sodium nitrate with a trace amount and a void volume with a large amount of it. A number of studies on retention mechanism of reversed-phase liquid chromatography have been carried out using the void volume determined by these methods.

In this study, the pulse response method was applied for determining a void volume of the ODS column. Correlation of elution volume with volumetric fraction of methanol in a mobile phase is shown in Figure 2. When the fraction of methanol is 70 vol. % and above, the elution volume of sodium nitrate, uracil, and methanol was almost equal. Both uracil and methanol were retained by ODS particles under the conditions that the concentration of methanol was lower than about 60 vol. %. The elution volume of the two substances increased with a decrease in the fraction of methanol in mobile phase. A constant value of the void volume was observed by introducing a large amount of sodium nitrate. In this study, the void volume of the ODS column was determined by the pulse response method with sodium nitrate.

Experimental data: gas- vs. liquid-phase adsorption

Experimental results are summarized in Table 3. Adsorption equilibrium constants and isosteric heats of adsorption in liquid-phase adsorption were smaller than those in gaseous systems for all adsorbates used in this study at 298 K. The ratio of adsorption equilibrium constant of ethylbenzene in the liquid-phase adsorption to that in the corresponding gaseous system was less than 1/700. The magnitude of activation energy of surface diffusion was almost the same in both gas- and liquid-phase adsorption systems.

Table 3. Comparison of Liquid- and Gas-Phase Adsorption

	Liquid Phase			Gas Phase		
Adsorbate	ln K	Qst (kJ/mol)	Es (kJ/mol)	ln K	Qst (kJ/mol)	Es (kJ/mol)
Benzene	0.73	6.7	19.4	6.08	35.3	13.5
Toluene	1.28	8.7	20.5	7.42	40.7	17.5
Ethylbenzene	1.75	9.7	22.0	8.30	43.8	23.2
p-Xylene	1.87	10.3	23.4	8.48	44.6	21.1
n-Pentane	2.35	11.8	—	4.66	31.7	10.2
n-Hexane	2.90	12.6	—	5.75	33.4	14.1
n-Heptane	3.43	14.8	—	6.94	38.2	14.4
n-Octane	3.98	17.2	—	8.16	43.4	17.1
Cyclohexane	2.45	10.4	22.2	5.92	33.0	15.6
Chrolobenzene	1.20	8.1	22.6	7.74	40.5	25.7

In liquid-phase adsorption activation energy of surface diffusion was found to be larger than isosteric heat of adsorption. Same experimental results have been reported for surface diffusion phenomena in liquid-phase systems (Awum et al., 1988; Ching et al., 1989; Ma et al., 1988; Miyabe and Suzuki, 1992, 1993a, 1994). These conditions suggest the following unreasonable situation, that is, it is energetically advantageous for adsorbed molecules to desorb from the surface to the bulk phase rather than to migrate on the surface and deny the presence of surface diffusion phenomena. On the other hand, the ratios of activation energy of surface diffusion to isosteric heat of adsorption are ranging from 0.4 to 0.6 in gaseous systems. These values agree with other experimental results reported for surface diffusion (Awum et al., 1988; Chihara et al., 1978; Gilliland et al., 1974; Kawazoe et al., 1974; Ruthven and Doetsch, 1976; Schneider and Smith, 1968; Sladek et al., 1974; Miyabe and Suzuki, 1993b).

In previous articles (Miyabe and Suzuki, 1992, 1993a), we reported properties of adsorption of *p*-tert-octylphenol onto the surface of ODS in a reversed-phase liquid chromatographic system. Quantitative analysis of adsorption data by the solvophobic theory showed that isosteric heat of adsorption was significantly influenced by the presence of a solvent. As shown in Table 3, the values of adsorption equilibrium constant and isosteric heat of adsorption in liquid-phase adsorption are apparently small compared with the corresponding results in gaseous systems. This study attempted to analyze the effect of a solvent on adsorption properties in the liquid-phase system by applying the solvophobic theory.

Estimation of calculation parameters of the solvophobic theory

Equation 30 includes three parameters which significantly influence the results analysis of the solvophobic theory. Estimation methods of the parameters, namely reduction of hydrophobic surface area due to adsorption, parameter κ^e, and molecular-size parameter, were studied in a wide range of methanol compositions.

Reduction of hydrophobic surface area

First moments of chromatographic peaks were analyzed according to the method of moment (Suzuki, 1973, 1990). Adsorption equilibrium constants were determined from the slope of linear relations between $(\mu_1 - t_0)/(1-\epsilon)$ and z/u_0. Isosteric heat of adsorption was determined from temperature dependence of adsorption equilibrium constants.

Adsorption equilibrium constants were plotted against mobile-phase composition in Figure 3. Logarithm of adsorption

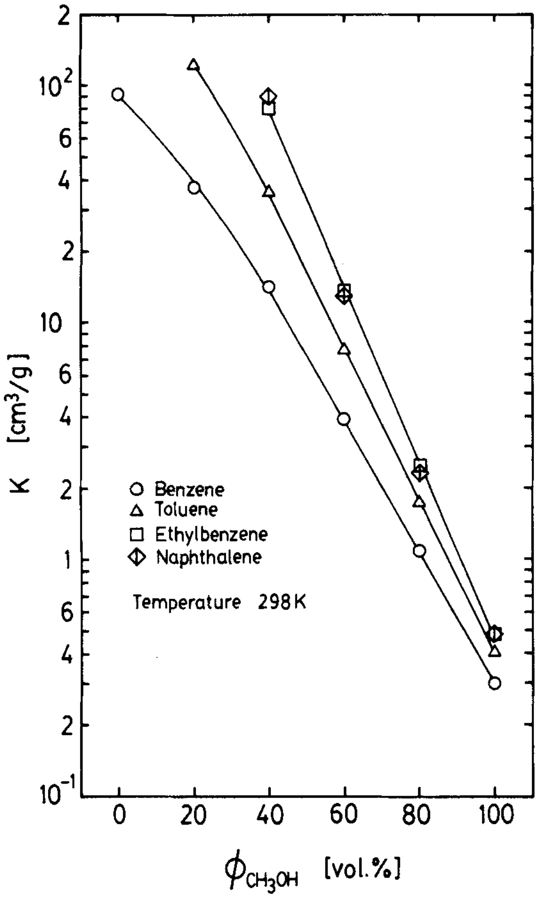

Figure 3. Correlation of the logarithm of adsorption equilibrium constant with methanol composition of the mobile phase.

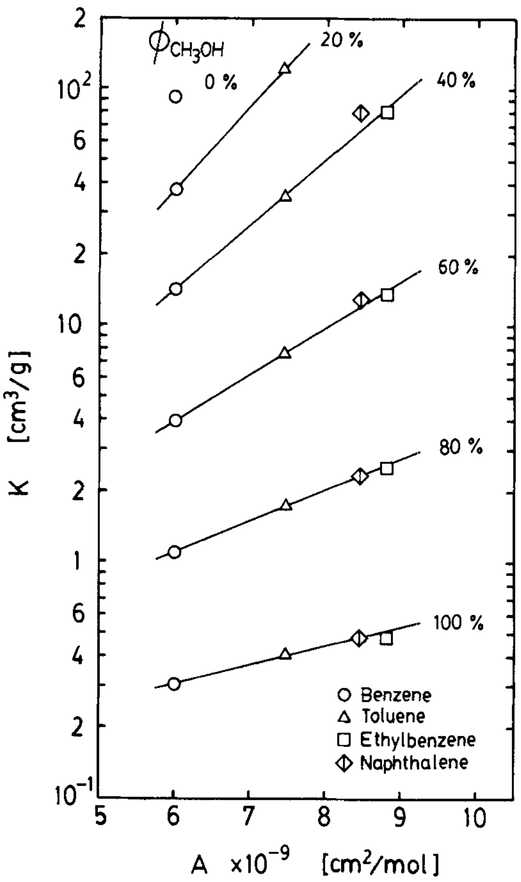

Figure 4. Correlation of the logarithm of adsorption equilibrium constant with the hydrocarbonaceous surface area of adsorbates.

Methanol composition was changed in the range from 0 to 100 vol. %.

equilibrium constant linearly increased with decreasing of the fraction of methanol. When the fraction of methanol was 40 vol. % and below, the slope of the linear relation decreased. This study attempted to quantitatively analyze the change in adsorption equilibrium constant accompanied by variation of mobile-phase composition applying the solvophobic theory.

Horvath et al. (1976) attempted to quantitatively explain the effect of a solvent on the retention behaviors in reversed-phase liquid chromatography by the solvophobic theory, when the decrease in a contact area between polar solvent and the hydrophobic surface of an adsorbate and an octadecyl ligand resulting from adsorption of the adsorbate on the stationary phase is regarded as a driving force of the retention behaviors. The magnitude of the decrease in the hydrophobic surface area is assumed to be proportional to that of the adsorbate. Horvath et al. confirmed linear relations between the logarithm of capacity factor and the surface area of adsorbates for three kinds of homologues. From the slope of the linear plots, Horvath et al. suggested that the proportionality constant was about 35% of a hydrocarbonaceous surface area for the reversed-phase liquid chromatographic separation of several organics. The ratio was also estimated as 20–30% of the solute total cavity surface area (Belfort et al., 1984).

In this study, experimental data in liquid-phase adsorption were analyzed in the same way proposed by Horvath et al. (1976). Adsorption equilibrium constants were plotted against the hydrophobic surface area of adsorbates in Figure 4, where the ratio was estimated from the slope of the linear plots. The slope of the plots increased with a decrease in methanol fraction in mobile phase. The ratio of ΔA to surface area of adsorbates was estimated to be 20–25% for 80–100 vol. % methanol/water mixture and about 40% for 0–20 vol. % methanol. Total surface area of adsorbates was calculated by summing the surface area increments of each group constituting the adsorbate molecule (Bondi, 1964).

Figure 5 shows correlations of adsorption equilibrium constant at 298 K with the surface area of several kinds of adsorbates. Methanol/water (70/30 by vol.) mixture was used as a mobile phase. Linear relations were observed for the homologous compounds such as *n*-alkanes, *n*-alkylbenzenes, *p*-*n*-alkylphenols, and *n*-alcohols. The parallel relations in Figure 5 suggest that the contribution of a methylene group to the adsorption equilibrium constant is almost identical irrespective of the structure and the kind of the adsorbates. Adsorption equilibrium constant increased by a factor of about 1.8 by adding one methylene group to an adsorbate molecule. The effect of introduction of one hydroxyl group to an ad-

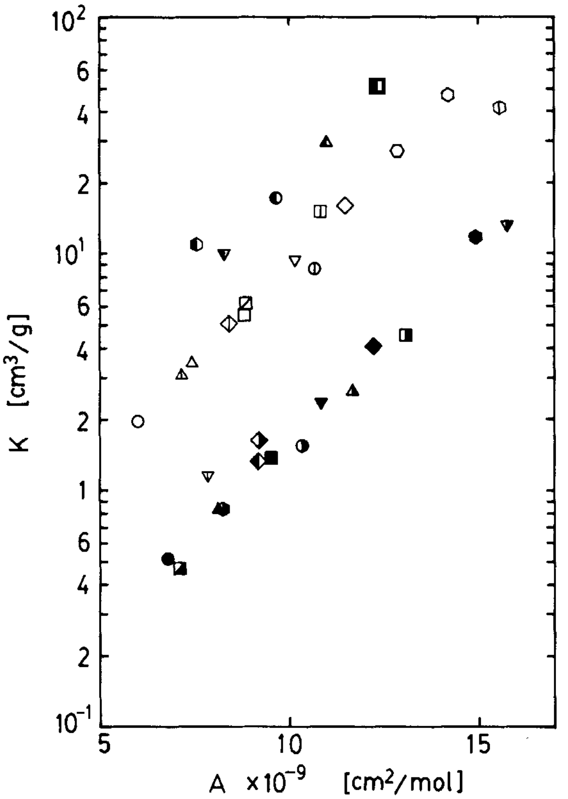

Figure 5. Correlation of the logarithm of adsorption equilibrium constant with the hydrocarbonaceous surface area of adsorbates.

Methanol composition was 70 vol. %.

Key	Adsorbate	Key	Adsorbate
○	Benzene	◭	*n*-Heptane
△	Toluene	◧	*n*-Octane
□	Ethylbenzene	◑	cyclo-Hexanol
▽	*n*-Propylbenzene	◐	cyclo-Hexane
◇	*n*-Butylbenzene		
○	*n*-Amylbenzene	⦶	Biphenyl
○	*n*-Hexylbenzene	◈	Naphthalene
⊠	*p*-Xylene	⬗	1-Naphthol
		⬖	2-Naphthol
●	Phenol		
▲	*p*-Cresol	⦶	Binaphthyl
■	*p*-Ethylphenol	⊞	Anthracene
▼	*p*-*n*-Propylphenol	▽	Nitrobenzene
◆	*p*-*n*-Butylphenol	△	Chlorobenzene
●	*p*-*n*-Hexylphenol	◪	Aniline
		⊖	Acetophenone
◑	*n*-Hexanol	⊟	Methylacetophenone
◭	*n*-Heptanol	⬘	Ethylacetophenone
◧	*n*-Octanol	⊖	Methylbenzoate
▼	*n*-Decanol	⬓	Ethylbenzoate
▼	*n*-Pentane	⬙	*n*-Propylbenzoate
◐	*n*-Hexane		

sorbate molecule on the adsorption equilibrium constant corresponded to that resulting from the decrease of about three or five methylene groups. The ratio of ΔA to surface area of adsorbates was estimated to be 30–35% for 70 vol. % methanol from the slope of linear plots in Figure 5.

Parameter κ^e

The parameter κ^e was introduced to correct the difference in enthalpy changes for the formation of a curved surface (cavity) in a solvent and a plane one having a same surface area. Horvath et al. (1976) estimated the value of κ^e in such a way that the calculation provided similar results to chromatographic data experimentally measured, and change in the parameter κ^e stems from change in mobile phase composition, as illustrated in Figure 6. A maximal value of κ^e was observed with methanol fractions in the region of 30–40 vol. %. The value of κ^e for 70 vol. % methanol was estimated as 2.1.

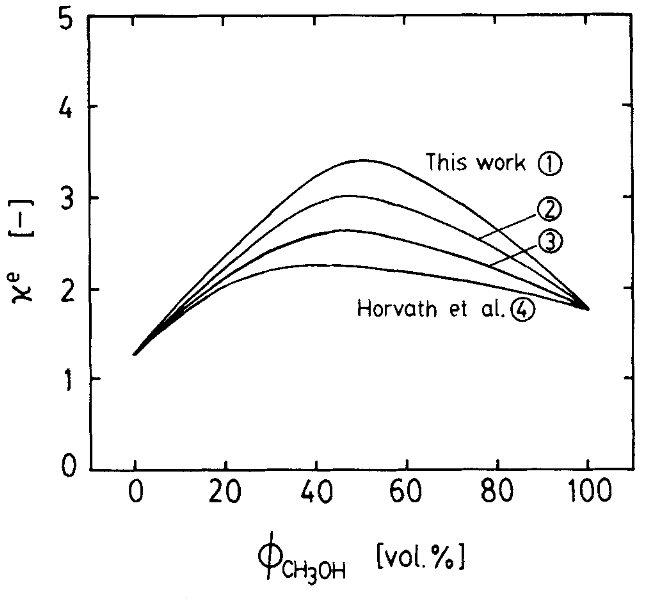

Figure 6. Dependence of κ^e on the composition of methanol/water mixtures at 298 K.

Vaporization process corresponds to formation of a cavity of one solvent molecule in the solvent. Value of κ^e can be correlated with the heat of vaporization of the solvent by:

$$\Delta H_v = \kappa^e A \gamma N[1-(d\ln\gamma/d\ln T)-2aT/3] \qquad (32)$$

A heat of vaporization was estimated to be about 2.5 times of an activation energy of viscosity by the absolute rate theory. For water and methanol, the ratio of ΔH_v to an activation energy of viscosity is about 2.5. In this study, the value of κ^e for methanol/water mixed solvents was estimated from an imaginary heat of vaporization calculated from an activation energy of viscosity of the mixtures. Resultant values of κ^e are illustrated in Figure 6. Though the tendency of change in κ^e due to change in methanol composition is similar to the results reported by Horvath et al. (1976), somewhat large values were obtained for κ^e. The value of κ^e estimated for 70 vol. % methanol was about 3.0.

As shown in Figure 6, similar values of κ^e were obtained by two quite different ways. The parameter κ^e seemed to have such a figure. There are, however, some subjects for the estimation of the parameter κ^e. For example, the shape of a cavity is assumed to be sphere because of the convenience of calculation, although there are various shapes and curvatures of the cavity depending on the properties of adsorbates. It seems that the solvent composition near an adsorbate

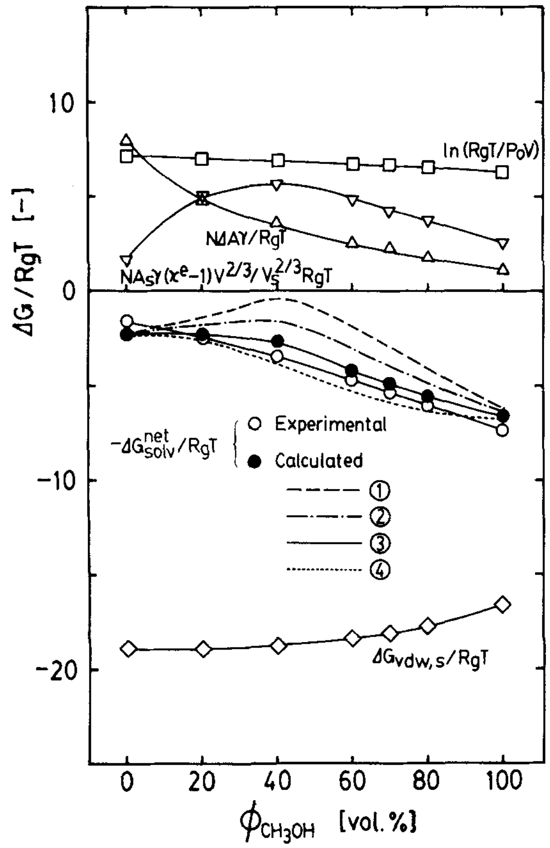

Figure 7. Effect of solvent on the free energy change of liquid-phase adsorption on ODS.

Solvophobic contributions of the individual terms to $\Delta G_{solv}^{net}/R_gT$ for benzene are plotted as a function of the composition of methanol in the mobile phase.

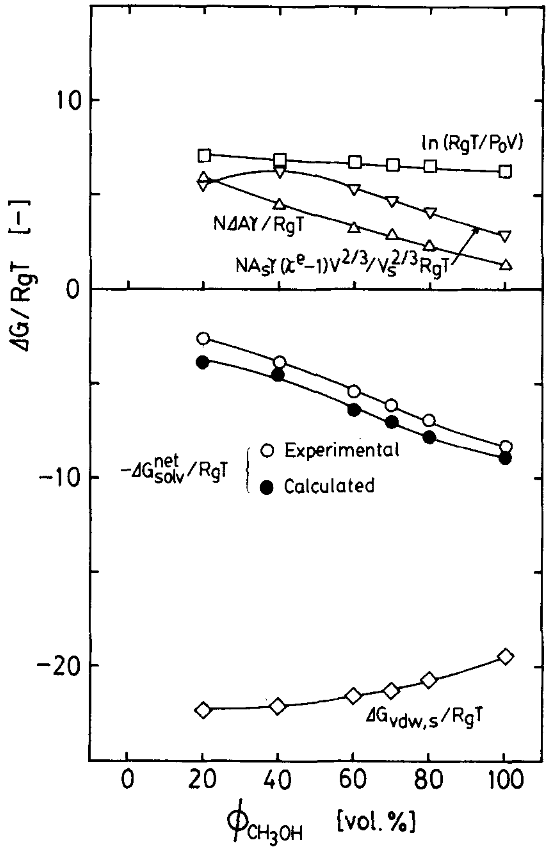

Figure 8. Effect of solvent on the free energy change of liquid-phase adsorption on ODS.

Solvophobic contributions of the individual terms to $\Delta G_{solv}^{net}/R_gT$ for toluene are plotted as a function of the composition of methanol in the mobile phase.

molecule is different from the composition in the bulk mobile phase, however, the difference in the solvent composition is not considered. A strict calculation method of the parameter κ^e based on physical consideration has not been proposed. Appropriate values of κ^e were estimated over a wide range of methanol composition in such a way that calculation results agreed with experimental data.

The value of ΔG_{solv} for benzene calculated by Eq. 30 was compared with experimental data in Figure 7. Calculation was carried out by taking the proportionality constant obtained from Figure 4 for each methanol composition. More accurate results could be obtained by using the estimation method of molecular-size parameter proposed by Tee et al., as mentioned later in this article. When the value of κ^e was taken according to the curve 3 in Figure 6, calculation results agreed with experimental data in a wide range of methanol fractions. The contributions of each term in Eq. 30 to the calculation results could also be evaluated separately.

Figure 8 shows a similar result for toluene. Though differences between calculation results and experimental data were observed, the trend of the correlation could be explained. It is concluded that the effect of solvent composition on free energy change in liquid-phase adsorption could be analyzed quantitatively by the solvophobic theory.

Molecular-size parameter

Horvath et al. (1976) and Belfort et al. (1984) employed Eqs. 16 and 17 to estimate molecular-size parameters. Tee et al. (1966) proposed a method based on the corresponding states correlation to estimate coefficients of the Kihara potential function from second virial coefficient and viscosity measured experimentally:

$$a^* = 0.15 + 2.37\omega_i \tag{33}$$

$$\sigma_i'(P_c/T_c)^{1/3} = 2.26 - 0.86\omega_i \tag{34}$$

$$l_i = a_i^*\sigma_i'/(1 + a_i^*) \tag{35}$$

$$\sigma_i = \sigma_i' - l_i \tag{36}$$

The molecular-size parameters of some organics estimated by the two methods are listed in Table 4, where the values of acentric factor are also shown. The figures of parameters l and σ calculated by the method proposed by Tee et al. were smaller than those estimated by the other method. The difference was found to range from 0.2 to 0.6 and increased with an increase in molecular size. On the other hand, the method reported by Horvath et al. provided smaller values for the mobile phase.

Table 4. Comparison of Molecular-Size Parameters Estimated by the Two Methods

		Horvath et al.			Tee et al.		
Adsorbate	ω	r	l $\times 10^8$ (cm)	σ	r	l $\times 10^8$ (cm)	σ
Benzene	0.212	5.72	2.09	3.23	5.72	1.86	2.85
Toluene	0.257	6.07	2.45	3.22	6.07	2.14	2.82
Ethylbenzene	0.301	6.36	2.79	3.18	6.36	2.38	2.75
p-Xylene	0.324	6.37	2.90	3.09	6.37	2.48	2.70
Chlorobenzene	0.249	5.97	2.37	3.20	5.97	2.11	2.85
n-Pentane	0.251	6.24	2.49	3.34	6.24	2.12	2.84
n-Hexane	0.296	6.50	2.83	3.27	6.50	2.38	2.79
n-Heptane	0.351	6.75	3.20	3.17	6.75	2.64	2.69
n-Octane	0.394	6.99	3.49	3.12	6.99	2.86	2.63
Cyclohexane	0.213	6.10	2.23	3.45	6.10	1.98	3.01
CH_3OH/H_2O (70/30, vol.)	0.0602	3.90	0.70	2.85	3.90	0.84	2.88

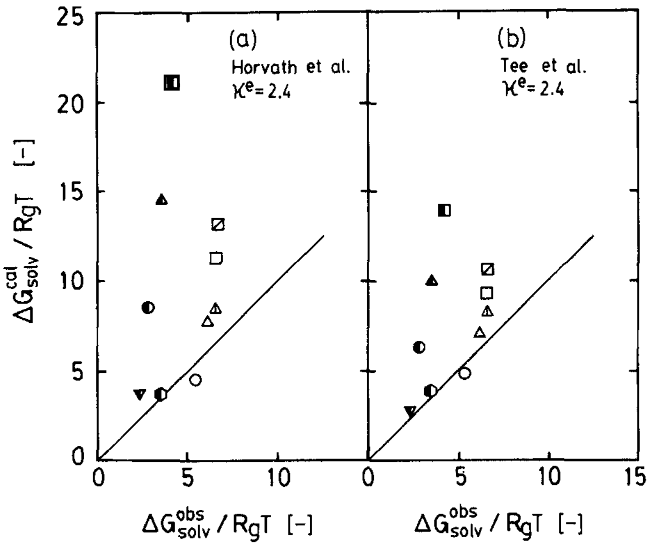

Figure 9. Effect of solvent on the free energy change of liquid-phase adsorption.

Keys refer to Figure 5.

Quantitative analysis of solvent effect on adsorption equilibrium in liquid-phase adsorption

The values of ΔG_{solv} calculated by Eq. 30 are compared with experimental data in Figure 9. Methanol/water mixture (70/30 by vol.) was used as a mobile phase. The decrease of hydrophobic surface area due to adsorption was assumed to be 35% of surface area of adsorbates. The value of κ^e was taken as 2.4, which was estimated from line 3 in Figure 6.

Figure 9 illustrates that the estimation method of molecular-size parameter proposed by Horvath et al. provides more scattered results. Both methods of Horvath et al. and Tee et al., however, gave same results for benzene and cyclohexane, which were small and compact molecules. An agreement was observed between ΔG_{solv} calculated and experimental data for small and compact molecules such as benzene and cyclohexane. It is concluded that solvent effect on free energy change in liquid-phase adsorption could be quantitatively analyzed by applying the solvophobic theory.

However, a poor correlation between the observed and the calculated free energy changes was also observed for adsorbates, which have relatively long alkyl chains in a molecule. The discrepancy seems to be due to calculation errors in estimation of parameters of the solvophobic theory. For example, a shape of an adsorbate and a cavity in which the adsorbate would be placed was assumed to be sphere because of the convenience of calculations. The shape and curvature of an adsorbate and a cavity surface are, however, irregular depending on properties of the adsorbate. Calculation errors resulted from the assumption in shape of the adsorbate and a cavity increased with an increase in alkyl chain length in an adsorbate. If the parameters of the solvophobic theory can be estimated by taking into account a real shape of an adsorbate and a cavity, one may obtain more accurate calculation results.

The contributions of each term in Eq. 30 to free energy change in liquid-phase adsorption are listed in Table 5. These data corresponded to the calculation results in Figure 9b. Deviation between experimental data and calculation results were relatively small for some compact molecules. The contributions of cavity formation and entropy change were almost equal. The role of van der Waals interaction was important and the contribution of electrostatic interaction was negligibly small in the hydrophobic adsorption phenomenon on the surface of ODS. Calculation errors increased with an increase in length of alkyl chain.

Relationship between adsorption equilibrium constant and solvent effect in liquid-phase adsorption

The adsorption equilibrium constant, K_{liq}, is expressed as follows from Eqs. 2 and 30 and must be correlated with a solvent effect, ΔG_{solv}, in liquid-phase adsorption:

Table 5. Comparison of Solvophobic Contributions

			Solvophobic Free Energy Change (kJ/mol)					
Adsorbate	ln K_{gas}	ln K_{liq}	ΔG_{solv}^{obs}	VDW	ES	CAV	CRAT	ΔG_{solv}^{cal}
Benzene	6.08	0.73	13.3	45.0	0	−16.4	−16.5	12.1
Toluene	7.42	1.28	15.2	52.8	0.02	−18.8	−16.5	17.5
Ethylbenzene	8.30	1.75	16.3	60.5	0.02	−21.0	−16.5	23.0
p-Xylene	8.48	1.87	16.4	64.0	0.02	−21.0	−16.5	26.5
n-Pentane	4.66	2.35	5.8	43.8	0	−20.2	−16.5	7.0
n-Hexane	5.75	2.90	7.1	54.5	0	−22.4	−16.5	15.6
n-Heptane	6.94	3.43	8.7	65.6	0	−24.4	−16.5	24.7
n-Octane	8.16	3.98	10.4	77.4	0	−26.4	−16.5	34.5
Cyclohexane	5.92	2.45	8.6	45.1	0.01	−18.9	−16.5	9.7
Chlorobenzene	7.74	1.20	16.2	55.3	0.38	−18.4	−16.5	20.7

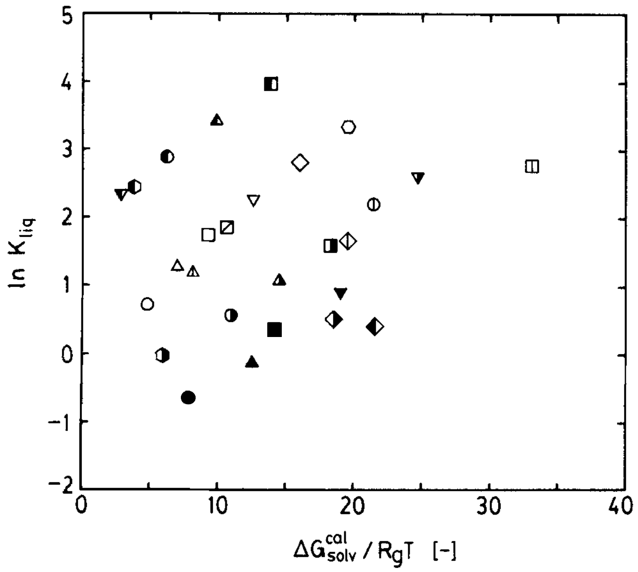

Figure 10. Correlation of the logarithm of adsorption equilibrium constant with the free energy change of liquid-phase adsorption.

Keys refer to Figure 5.

$$\ln K_{liq} = (-\Delta G_{solv}/R_gT) - (\Delta G_{gas}/R_gT) \qquad (37)$$

Belfort et al. (1984) theoretically studied liquid-phase adsorption of several organics such as alcohols and ketones onto an activated carbon from aqueous solution by the solvophobic theory. Adsorbability of the adsorbates could be correlated with a solvent effect on free energy change in liquid-phase adsorption. Belfort et al., however, carried out the solvophobic calculation by using intact parameters which were proposed by Horvath et al. (1976). The experimental systems which Belfort et al. studied were different from those of reversed-phase liquid chromatography.

Figure 10 shows the correlation of adsorption equilibrium constants experimentally measured with ΔG_{solv} calculated for several kinds of organics in reversed-phase liquid chromatographic systems. Separate linear relations were observed for each homologue. As shown in Figure 9, the value of ΔG_{solv} increases with an increase in molecular size of adsorbates. The magnitude of a reduction in ΔG_{gas} seemed to be larger than the increment of ΔG_{solv}. It was clarified that adsorbability (retention behavior) of adsorbates could be estimated from the value of ΔG_{solv} for each homologue in a reversed-phase liquid chromatographic system.

Quantitative analysis of solvent effect on isosteric heat of adsorption in liquid-phase adsorption

Quantitative analysis was attempted to explain the solvent effect on isosteric heat of adsorption in a similar way by Eq. 31. Calculation results are shown in Figure 11. Though the tendency of the plots are similar to those in Figure 9 on the whole, large deviation between experimental data and calculation results are observed even when benzene and cyclohexane were used as an adsorbate. The calculation errors apparently result from the uncertainty in the estimation of temperature dependence of calculation parameters and enthalpy change of van der Waals interaction.

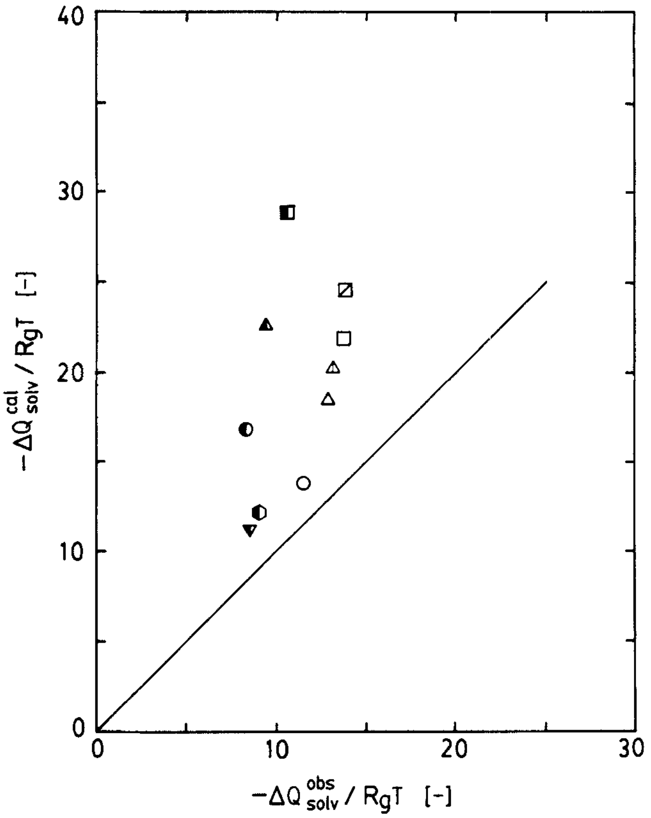

Figure 11. Effect of solvent on the enthalpy change of liquid-phase adsorption.

Keys refer to Figure 5.

As shown in Eq. 31, information about temperature dependence of two parameters, namely surface tension of a solvent and the parameter κ^e, was required in order to quantitatively analyze the effect of solvent on isosteric heat of adsorption. Temperature dependence of surface tension of methanol/water mixture was calculated from the values which were estimated at different temperatures by using the equation proposed by Tamura et al. (Ried et al., 1977). On the other hand, there is no information about change in κ^e of methanol/water mixture with respect to temperature. According to Eq. 32, temperature dependence of κ^e may be calculated from the values of heat of vaporization estimated at given temperatures by using Riedel equation (Ried et al., 1977). Temperature dependence of the two parameters obtained in this way may have uncertain results.

Sinanoglu et al. (1969) and Horvath et al. (1976) used Eq. 7 for estimating free energy change, which resulted from van der Waals interaction based on dispersion forces. In Eq. 7, a shape of an adsorbate and a cavity in which the adsorbate would be placed was assumed to be sphere because of convenience of calculations. The shape and curvature of an adsorbate and a cavity surface are, however, irregular depending on properties of an adsorbate. Calculation errors resulted from the assumption in shape of an adsorbate and a cavity increased with an increase in alkyl chain length in an adsorbate. The poor correlation between the observed and the calculated free energy changes for some adsorbates which contain an alkyl chain in a molecule seems to be attributed to the calculation errors. If the parameters of the solvophobic theory can be estimated by taking into account a real shape of an adsorbate and a cavity, one may obtain more accurate calculation results. The discrepancy between calculation results and experimental data seems to result from the uncertainties in the estimation of temperature dependence of the two parameters, namely surface tension and κ^e of a mixed solvent with the assumption that the shape of adsorbates and cavities is sphere. Further investigation must be necessary for this subject. It was, however, confirmed that isosteric heat of adsorption was influenced by a solvent and that an apparent small value was observed as Q_{st} in liquid-phase adsorption systems.

Conclusion

The effect of a solvent on adsorption characteristics in liquid-phase adsorption was studied.

The pulse response method was evaluated for determining a void volume of an ODS column. As an inert substance, sodium nitrate, uracil, and methanol were employed. When the fraction of methanol was 70 vol. % and above, the elution volume of the three substances was almost equal. Both uracil and methanol, however, were retained by ODS particles under the conditions that the fraction of methanol was lower than about 60 vol. %. The elution volume of the two substances increases with a decrease in the fraction of methanol in a mobile phase. A constant value of a void volume was observed under the conditions that a large amount of sodium nitrate was introduced into the column.

In liquid-phase adsorption, isosteric heat of adsorption was found to be smaller than activation energy of surface diffusion. It must be easier for adsorbed molecules to desorb into a bulk phase than to migrate on a surface under such conditions. As a result of the comparison of adsorption data for several organics in both gas- and liquid-phase adsorption systems, it was experimentally confirmed that the adsorption equilibrium constant and isosteric heat of adsorption in liquid-phase adsorption were smaller than those in a corresponding gaseous system and that the apparently unreasonable situation was a result of the influence of a solvent.

It was attempted to quantitatively explain the solvent effect on adsorption equilibrium by the solvophobic theory. Estimation methods were investigated for three parameters of the theory, that is, molecular-size parameter, reduction of hydrophobic surface area accompanied by adsorption, and parameter κ^e, which extremely influence the calculation results of the solvophobic theory.

Adsorption equilibrium constant was increased by adding a hydrophobic increment such as methylene group or phenyl ring. On the other hand, an introduction of hydroxyl group into an adsorbate molecule decreased adsorption equilibrium constant. From the correlation between adsorption equilibrium constant and surface area of adsorbates, the decrease in hydrophobic surface area exposed to a polar solvent resulting from adsorption was estimated as 30–35% of the total surface area of the adsorbate molecule when methanol/water mixture (70/30 by vol.) was employed as a mobile phase. Similarly, the ratio of ΔA to surface area of adsorbates was estimated to be 20–25% for 80–100 vol. % methanol/water mixture and 40% for 0–20 vol. % methanol from the correlation of adsorption equilibrium constant with surface area of adsorbates, illustrated in Figure 4.

Logarithm of adsorption equilibrium constant linearly increased with a decrease in fraction of methanol. When the fraction of methanol was 40 vol. % and below, the slope of the linear relation decreased. This feature of change in adsorption equilibrium constant could be interpreted by the solvophobic theory. The effect of solvent composition on free energy change in liquid-phase adsorption could be quantitatively analyzed by applying the solvophobic theory. It was suggested that appropriate values of κ^e could be obtained from curve 3 in Figure 6.

Two methods for estimation of molecular-size parameter were evaluated. Both methods proposed by Horvath et al. (1976) and Tee et al. (1966) provided almost same results for benzene and cyclohexane, which were small and compact molecules. However, the method of Horvath et al. showed more scattered calculation results for the other adsorbates which have an alkyl chain in the molecule.

The solvent effect on adsorption equilibrium constants could be quantitatively analyzed by the solvophobic theory. The calculation results agreed with experimental data for a compact molecule such as benzene and cyclohexane. The contributions of each term, which influence free energy change in liquid-phase adsorption, could be evaluated separately.

It was clarified adsorbability (retention behavior) of adsorbates could be estimated from value of ΔG_{solv} for each homologue in reversed-phase liquid chromatographic systems.

Solvent effect on isosteric heat of adsorption could not be interpreted satisfactorily in this study. It was, however, confirmed that isosteric heat of adsorption was influenced by a solvent and that an apparent small value was observed as Q_{st} in liquid-phase adsorption systems. Several subjects still remain to be clarified in regard to the accurate estimation of calculation parameters in the solvophobic theory.

Notation

a = coefficient of thermal expansion, cm^3/K
a^* = defined by Eq. 33
A = surface area, cm^2
CAV = cavity formation
CRAT = cratic term
d_p = particle diameter, μm
D = Clausius-Mosotti function, Eq. 9
Ds = surface diffusion coefficient, cm^2/s
ES = electrostatic interaction
Es = activation energy of surface diffusion, kJ/mol
G = Gibbs free energy, kJ/mol
ΔH_v = heat of vaporization, kJ/mol
I = ionization potential, eV
k' = capacity factor
k^2 = tortuosity factor
K = adsorption equilibrium constant, cm^3/g
l = Kihara parameter, cm
n = refractive index
N = Avogadro's number
P = defined by Eq. 20
P_c = critical pressure, Pa
P_0 = pressure, Pa
Q = defined by Eq. 10
ΔQ = defined by Eq. 31
Q_{st} = isosteric heat of adsorption, kJ/mol
r = solute diameter, cm

R_g = gas constant
t' = defined by Eq. 11
T = temperature, K
T_c = critical temperature, K
u_0 = superficial velocity, cm/s
V = molar volume, cm^3/mol
V_e = elution volume, cm^3
VDW = van der Waals interaction
W = cavity formation, Eq. 5

Greek letters

α = polarizability, cm^3
γ = surface tension, dyn/cm
Δ = defined by Eq. 8
ϵ = void fraction of a column
ϵ_p = porosity
ϵ' = dielectric constant of solvent
ϵ_0 = free space permittivity constant
κ^e = energy correction for curved surface
κ^s = entropy correction for curved surface
λ = proportionality constant in Eq. 27
μ = dipole moment
ν = molecular volume, cm^3
ρ_p = particle density, g/cm^3
σ = London diameter, cm
ϕ = volumetric fraction of organic modifier in mobile phase, %
ψ = defined by Eq. 19
ω = acentric factor

Subscripts

av = arithmetic mean parameter
cav = cavity formation
es = electrostatic interaction
gas = gas-phase reaction
i = ith species
liq = liquid-phase reaction
S = solute
solv = solvent
vdw = van der Waals interaction

Superscripts

cal = calculation result
net = sum of all interactions
obs = experimental data

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