

# Effects of Residual Silanol on Solid Phase Extraction of Organic Compounds to Octadecylsilyl Silica

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Batchwise equilibrium study was carried out on the retention of nonpolar and polar organic compounds to octadecylsilyl (ODS) silicas of different properties at atmospheric pressure. While nonpolar compounds were retained only by distribution on the ODS phase, polar compounds were retained by both distribution and Langmuir-type adsorption on residual silanol. Retention on ODS silica with more silanol proceeded at a higher rate than retention on ODS silica with less silanol and was reversible on this solid phase extraction time-scale. An increase in surface density of ODS decreased the distribution constant, due to a decrease in fraction of ODS functioning as an extracting medium and also decreased the saturated adsorption amount, due to reductions of the residual silanol and the functioning ODS. The ODS silica with the lowest ODS density showed a distribution constant 31 times higher and a saturated adsorption amount 27 times higher than the ODS silica with the highest ODS density. On the other hand, because the interaction between the organic part and the ODS group introduced at higher density is strengthened, the adsorption constant is increased by about 5 times compared to the low density ODS silica. The electronic effects of substituents to nitrogen- and oxygen-containing compounds on retention were discussed. In conclusion, ODS silica with an appreciable amount of residual silanol is superior for solid phase extraction.

**Keywords** Solid phase extraction, octadecylsilyl silica, residual silanol, langmuir adsorption, distribution, nitrogen or oxygen-containing reagents

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## Introduction

Octadecylsilyl (ODS) silica has been developed as a packing material for reversed phase liquid chromatography (RPLC).<sup>1,2</sup> Disappearance or severe tailing of basic compounds' peaks observed in the initial stage of the development was attributed to the interaction of a basic functional group with residual silanol. These drawbacks were overcome by end-capping (EC) treatment with a trimethylsilyl (TMS) group or by thermal dehydration of base silica prior to introduction of long alkyl groups;<sup>3-6</sup> columns without any problems in this respect are now commercially available. Silanol, however, does exist in such EC-ODS silica. It is recommended that the contribution of silanol to retention in RPLC both as the hydrogen-bond donor and acceptor, and the properties characterized by spectroscopy such as IR and CP/MAS <sup>29</sup>Si NMR<sup>3,6,7</sup> be taken into account.<sup>8</sup>

Accompanied with an increased surface density of alkyl groups on silica gel, reduction in retention or reduction in reproducibility of the retention time of RPLC became noticed in the use of a highly aqueous mobile phase; this was attributed to dewetting of or formation of a gas phase in micropores.

Increasing the back-pressure, increasing the pore size of silica gel, using a longer alkyl group, or embedding a hydrophilic anchor enhanced intrusion of a highly aqueous mobile phase into hydrophobic pores overcame such reductions.<sup>9-15</sup>

Recently, a new separation method using an ODS column with its micropores intentionally filled with a gas and an aqueous mobile phase operated at relatively low pressure has been proposed as surface-bubble-modulated liquid chromatography (SBMLC).<sup>16</sup> It had been pointed out experimentally and by molecular simulation that at least two factors, such as adsorption of an analyte at the alkyl-bonded layer/solvent interface and its distribution into the alkyl-bonded layer, contribute to the retention in RPLC.<sup>17,18</sup> Their contributions could, however, not be separated from each other experimentally, since the surface area of the alkyl-bonded layer/solvent interface and the volume of the alkyl-bonded layer had not been expected to be altered independently. Nakamura and others have succeeded in this separation by comparing retentions of a series of compounds on the same column operated both in the RPLC mode and the SBMLC mode and have quantitatively shown a large contribution of the adsorption to the retentions of hydrophilic compounds.<sup>16</sup> Furthermore, they have also succeeded in correcting the contribution of the EC silica surface to the retentions and have shown an excellent correlation of the corrected distribution coefficients with the distribution constants into neat hexadecane with regard to compounds of varying polarities.<sup>19</sup>

In parallel with the progress of RPLC, ODS silica has also been utilized as an extracting medium in solid phase extraction

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(SPE) for the preconcentration of target analytes and for the removal of foreign substances.<sup>20,21</sup> Although the merit of residual silanol was recognized in SPE, EC-ODS silica has been adopted for actual use. As a result, the ODS silica is required to be conditioned with some water-miscible organic solvents such as methanol and acetonitrile prior to introduction of an aqueous sample solution.<sup>20</sup> Competitive retention of these solvents on ODS silica is thought to reduce the retention of analytes, or loss of these solvents by diffusion into aqueous solutions during flow treatment of a large volume sample is thought to lose the wetting function. A far fewer number of fundamental studies have been conducted on SPE under atmospheric pressure, than on RPLC. Freundlich-type adsorption of acetylacetone and Langmuir-type adsorption of phenanthroline were reported with regard to retention on ODS silica.<sup>22,23</sup>

In a previous work, we demonstrated that a hexadentate chelating reagent dissolved in toluene was retained on ODS silica as the sum (defined afresh as retention including isotherms within this paper) of the simple distribution to the ODS phase and the Langmuir adsorption to residual silanol group mechanism.<sup>24</sup> A large amount of the reagent could be retained on the ODS silica containing a large amount of residual silanol by virtue of the Langmuir adsorption term. In the retention of acetylacetone and its metal complex from the aqueous phase on the ODS phase, it was reported that the residual silanol group improves the wettability of the ODS phase and is the donor of the ligand and the metal complex.<sup>25</sup> In this study, a series of compounds with and without basic hetero atoms (nitrogen or oxygen) were retained on ODS silicas of varying characteristics. The effects of the silica pore size, the type and the density of ODS group and the end-capping on the performance of ODS silica as an extracting medium were evaluated from equilibrium points of view.

## Experimental

### Materials

Eight ODS silicas were prepared with base silicas of various pore sizes (50, 75, 100, 150, and 300 Å) according to the literature.<sup>26</sup> Each of the ODS silicas is abbreviated as the pore size and the modifying mode (P: polymeric; M: monomeric; E: end-capped): 50P, 75P, 100P, 150P, 300P, 50M, 300M, 50PE. These ODS silicas and the corresponding base silicas (50S, 75S, 100S, 150S, 300S) were subjected to evaluation as needed.

Benzene (bz) and toluene (tl) were adopted as nonpolar compounds, while pyridine (py) and acetylacetone (Hacac) were adopted as polar compounds. With a view to verifying electronic and steric effects, 2,2'-bipyridine (bpy) and 2,6-lutidine (lu) were examined for comparison with py, and 3-pentanone (pt), 1,3-dichloroacetone (dca), cyclohexanone (chx), and 1,2-cyclohexanedione (chd) for comparison with Hacac.

### Physicochemical properties of ODS silicas

The physicochemical parameters of ODS silicas were evaluated using the results of elemental analysis (carbon contents) and the intrinsic parameters of base silicas as follows. In polymeric modification with trichlorooctadecylsilane ( $C_{18}H_{37}SiCl_3$ ), proton on silanol was finally replaced by  $[C_{18}H_{37}Si(OH)_2]$ -group [carbon number (CN) = 18, molecular weight (MW) = 315 g mol<sup>-1</sup>]. In monomeric modification with dimethyloctadecylchlorosilane ( $C_{18}H_{37}Si(CH_3)_2Cl$ ), proton was replaced by  $[C_{18}H_{37}Si(CH_3)_2]$ -group (CN = 20, MW = 311 g mol<sup>-1</sup>). In end-capping with trimethylchlorosilane ( $(CH_3)_3SiCl$ ), proton was replaced by  $[(CH_3)_3Si]$ -group (carbon number = 3,

molecular weight = 73 g mol<sup>-1</sup>). When the chemical amounts of ODS and TMS groups successively modified on 1 kilogram of base silica were defined as  $MD_{ODS}$  and  $MD_{TMS}$ /mol kg<sup>-1</sup>, the masses ( $w_{ODS}$ ,  $w_{EC}$ /kg) and carbon contents ( $CC_{ODS}$ ,  $CC_{EC}$ ) after modifications were given by Eqs. (1) – (4).

$$w_{ODS} = 1 + MD_{ODS} \times (MW - 1) \quad (1)$$

$$w_{EC} = 1 + MD_{ODS} \times (MW - 1) + MD_{TMS} \times (73 - 1) \quad (2)$$

$$CC_{ODS} = \frac{MD_{ODS} \times CN \times 12}{w_{ODS}} \quad (3)$$

$$CC_{EC} = \frac{MD_{ODS} \times CN \times 12 + MD_{TMS} \times 3 \times 12}{w_{EC}} \quad (4)$$

Thus, both  $MD_{ODS}$  and  $MD_{TMS}$  were obtained from  $CC_{ODS}$  and  $CC_{EC}$  of each ODS silica. The chemical amounts of ODS and TMS groups on 1 kilogram of modified ODS silicas,  $MD'_{ODS}$  and  $MD'_{TMS}$ /mol kg<sup>-1</sup>, were calculable by Eqs. (5) and (6), respectively.

$$MD'_{ODS} = \frac{MD_{ODS}}{w_{ODS}} = \frac{CC_{ODS}}{CN \times 12} \quad (5)$$

$$MD'_{TMS} = \frac{MD_{TMS}}{w_{EC}} \quad (6)$$

The surface areas of the silicas after modification ( $S_{ODS}$  and  $S_{EC}$ /m<sup>2</sup> g<sup>-1</sup>) were, on the other hand, respectively decreased from the surface area of base silica ( $S_0$ ) according to Eqs. (7) and (8).

$$S_{ODS} = \frac{S_0}{w_{ODS}} \quad (7)$$

$$S_{EC} = \frac{S_0}{w_{EC}} \quad (8)$$

The surface densities of ODS and TMS,  $SD_{ODS}$  and  $SD_{TMS}$ /μmol m<sup>-2</sup>, were thus given by Eqs. (9) and (10), respectively.

$$SD_{ODS} = \frac{MD'_{ODS}}{S_{ODS}} \times 1000 \quad (9)$$

$$SD_{TMS} = \frac{MD'_{TMS}}{S_{EC}} \times 1000 \quad (10)$$

The relative errors of SD were ±0.02 μmol m<sup>-2</sup>.

The water content ( $W$ /mmol g<sup>-1</sup>) of ODS silicas and silicas were determined by Karl-Fischer coulometry after equilibration in the atmosphere at 25°C and at relative humidity of 50% for a few days. The surface density of water,  $SD_w$ , was similarly calculated by Eq. (11).

$$SD_w = \frac{W}{S_{ODS} \text{ or } S_{EC} \text{ or } S_0} \times 1000 \quad (11)$$

The relative errors of  $SD_w$  were ±0.1 μmol m<sup>-2</sup>. All these parameters of ODS silicas are summarized in Table 1.

### Retention of organic compounds from aqueous phase to ODS silica

An aliquot of ODS silica or silica gel ( $m/g = 0.05$  or  $0.5$ , respectively) was shaken with aqueous solutions of organic compounds ( $C_R$ /mol L<sup>-1</sup> = 0.001 – 0.3,  $V/mL = 5$ ) at 25°C.

Table 1 Physicochemical properties of ODS silicas<sup>a</sup>

Abbreviation	CC <sub>ODS/EC</sub>	S <sub>ODS/EC/0</sub> /m <sup>2</sup> g <sup>-1</sup>	MD' <sub>ODS</sub> /mol kg <sup>-1</sup>	SD <sub>ODS</sub> /μmol m <sup>-2</sup>	SD <sub>w</sub> <sup>b</sup> /μmol m <sup>-2</sup>	(SD <sub>ODS</sub> + SD <sub>w</sub> ) <sup>b</sup> /μmol m <sup>-2</sup>
50S	0	680	0	0	10.6	10.6
50P	0.143	539	0.66	1.23	3.5	4.7
75P	0.204	387	0.94	2.44	4.3	6.7
100P	0.176	204	0.81	4.00	4.6	8.6
150P	0.137	117	0.63	5.42	5.1	10.5
300P	0.100	67	0.46	6.95	5.8	12.7
50M	0.183	519	0.76	1.47	5.1	6.6
300M	0.061	79	0.25	3.21	5.4	8.6
50PE <sup>c</sup>	0.168	501	0.62	1.23	1.1	4.3 <sup>d</sup>

a. Particle size/μm: 40 – 50 (50S, 50P, 50PE, 50M); 75 – 180 μm (75P, 100P, 150P, 300P, 300M). b. Error of ± 0.1. c. MD'<sub>TMS</sub> = 0.97 mol kg<sup>-1</sup>, SD<sub>TMS</sub> = 1.94 μmol m<sup>-2</sup>. d. SD<sub>ODS</sub> + SD<sub>TMS</sub> + SD<sub>w</sub>.

In all compounds, buffer solution was not added so as not to interfere with the retention. After equilibration, the UV spectra of the supernatant solutions were recorded to measure the concentrations in the aqueous phase, [R]/mol L<sup>-1</sup>. The retention of R to or the concentration of R in unit mass of ODS silica or silica gel, [R]<sub>s,obsd</sub>/mol kg<sup>-1</sup> was calculated by Eq. (12).

$$[R]_{s,obsd} = \frac{V \times (C_R - [R])}{m} \quad (12)$$

As stated in our previous work,<sup>24</sup> the retention of each compound on ODS is expressible as the sum of the simple distribution (Eq. (13)) and the Langmuir-type adsorption (Eq. (14)) as given by Eq. (15).

$$g([R]) = K_d \times [R] \quad (13)$$

$$h([R]) = \frac{K_{ad} A_{max} [R]}{1 + K_{ad} [R]} \quad (14)$$

$$[R]_{s,cald} = g([R]) + h([R]) \quad (15)$$

where  $K_d/L \text{ kg}^{-1}$  denotes the distribution constant of the aqueous phase to ODS silica,  $A_{max}/\text{mol kg}^{-1}$  represents the saturated adsorption amount, and  $K_{ad}/\text{mol}^{-1} \text{ L}$  denotes the adsorption constant of each compound. These constants were optimized to give minimum error sums on retention as given by Eq. (16).

$$U = \sum ([R]_{s,obsd} - [R]_{s,cald})^2 \quad (16)$$

The concentration of each compound in the solid phase defined by Eq. (12) was expressed as the chemical amount per unit mass of ODS silica. Using the mass fraction of ODS in ODS silica,  $r_{ODS}$ , given by Eq. (17), the intrinsic distribution constant relevant to the concentration in neat ODS without silica was recalculated by Eq. (18).

$$r_{ODS} = \frac{MD'_{ODS} \times 253}{1000} \quad (17)$$

$$K_d' = \frac{K_d}{r_{ODS}} \quad (18)$$

## Results and Discussion

### Physicochemical properties of ODS silica

Silica gel with the pore size of not less than 100 Å has

conventionally been used to prepare ODS silica by taking into account the elongated ODS group length of around 20 Å. Introduction of ODS group into silica gels with narrower pores (50 and 75 Å) was examined in this research and was achieved under comparable synthetic conditions as shown in Table 1. The ODS-silicas derived from silicas of such narrower pores, however, had appreciably lower surface densities than those of the wider pores. Moreover, 50P has a lower SD<sub>ODS</sub> than 50M in contrast to the general observation for silica of a wider pore size; actually, 300P showed a higher SD<sub>ODS</sub> than 300M even in this study. These suggest that polymerization did not occur so extensively with regard to 50P and more silanol groups thereby remained.

The surface density of silanol on silica gel has been reported to be around 8 μmol m<sup>-2</sup>.<sup>27</sup> The SD<sub>w</sub> values of silica gel determined at a relative humidity of 50% were in a range of 10 – 12 μmol m<sup>-2</sup> irrespective of the pore size: 10.6 for 50S, 10.1 for 75S, 9.5 for 100S, 10.8 for 150S, and 11.0 for 300S. This indicates that one or two water molecules interact with one of the densely located silanol groups on base silicas. The respective sums of SD<sub>ODS</sub> and SD<sub>w</sub> of 50M and 300M (6.6 and 8.8) were close to the surface density of silanol on silica gel; this suggests that each one water molecule interacts with one silanol group on these ODSs. Comparable sums were observed for 75P and 100P. In contrast, the sums for 150P and 300P were appreciably larger, since the enhanced polymerization increased SD<sub>ODS</sub> with no consumption of silanol on base silica and also increased the amounts of silanol to be hydrated. The sum for 50P was slightly low.

### Overview on retention

The time courses for retention of py on 50P and 50PE are shown in Fig. S1 (Supporting Information). The suspension of pyridine solution and ODS silica was stirred such that ODS silica did not float but came into contact with an aqueous py solution, especially for 50PE. An appreciably longer time was required to reach equilibrium for 50PE (15 min) than for 50P (5 min), in spite of less change in [py]. This is attributed to the water-repellent property of 50PE.<sup>9-15</sup>

Retention isotherms of bz and py to 50S, 50P, and 50PE are shown in Fig. 1 and others are given in Figs. S2 – S5 (Supporting Information). Benzene was scarcely retained on 50S but was appreciably retained on 50P only by distribution on the ODS phase. Pyridine was retained on 50S only by adsorption on the silanol group but was retained on 50P by both distribution and adsorption. In previous reports, the retention factors have been discussed in the low concentration region (up to 0.04 mol/L for acetylacetone and 0.006 mol/L for 1,10-phenanthroline),<sup>22,23</sup>

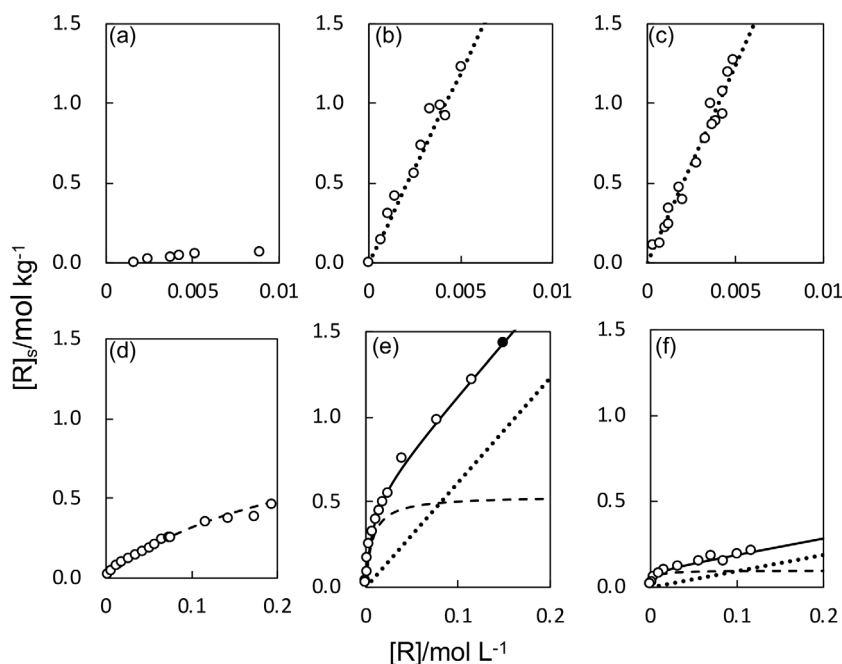


Fig. 1 Isotherms on retention of bz (a, b, c) and py (d, e, f) on 50S (a, d), 50P (b, e) and 50PE (c, f). Open: under atmospheric pressure, closed: under pressurized condition. Solid line: calculated by Eq. (15); dotted line: distribution term given by Eq. (13), broken line: Langmuir adsorption term given by Eq. (14).

Table 2 Retention parameters of organic compounds from aqueous phase on ODS silicas<sup>a,b</sup>

Abbreviation	R							
	bz		tl		py			
	log $K_d$	log $K_d'$	log $K_d$	log $K_d'$	log $K_d$	log $K_d'$	$A_{\max}$	log $K_{ad}$
50S	n.s.	n.s.	n.m.	n.m.	—	—	1.02(1)	0.66(2)
50P	2.38(4)	3.16(4)	3.06(3)	3.84(3)	0.79(2)	1.57(2)	0.54(2)	2.17(6)
75P	2.20(5)	2.82(5)	2.83(3)	3.45(3)	0.49(7)	1.11(7)	0.44(1)	2.40(3)
100P	2.14(2)	2.83(2)	2.64(1)	3.33(1)	0.15(3)	0.84(3)	0.21(1)	2.60(3)
150P	1.70(5)	2.49(5)	2.38(3)	3.17(3)	-0.3(1)	0.4(1)	0.07(1)	2.59(1)
300P	1.46(5)	2.39(5)	2.11(3)	3.04(3)	-0.85(5)	0.08(5)	0.02(0)	2.89(4)
50M	2.50(2)	3.17(2)	n.m.	n.m.	0.50(5)	1.17(5)	0.56(2)	1.90(5)
300M	1.73(1)	2.87(1)	n.m.	n.m.	-0.25(3)	0.89(3)	0.03(0)	2.58(2)
50PE	2.39(2)	3.20(2)	n.m.	n.m.	-0.03(5)	0.78(5)	0.10(1)	2.41(2)

a. Error in the last digit shown in parentheses. b. n.s.: negligibly small, n.m.: not measured.

but in this study, by measuring the higher concentration side, the compound is retained on the ODS silica by distribution on the ODS phase and adsorption on the residual silanol group. The retention mechanisms of bz and py on 50PE were respectively the same as those for 50P.

The relevant constants obtained by equilibrium analysis are summarized in Table 2 and others are given in Table S1 (Supporting Information); the calculated curves using these constants well reproduce the experimental points in any systems. The maximum retained sample amounted to several tens of mg. This corresponds to only 10% of the mass of ODS silica but is comparable to the mass of neat ODS. Such high sample concentrations, which are not achieved by dissolution in liquid alkanes, indicate the unique and superior property of ODS silica. This is reflected in that the distribution constants  $K_d'$  in the present study are larger by about one order of magnitude

than the distribution constants between water and hexadecane,<sup>28</sup> although the difference in the definition [the mass (kg) of ODS without the sample against the volume (L) of hexadecane with the sample] may also have a contribution.

It has recently been shown that the retentions of compounds in RPLC and SBMLC are governed by three mechanisms: retention on the alkyl-bonded layer/solvent interface, retention on the alkyl-bonded layer, and retention on the silica surface.<sup>16,19</sup> These are quantified as respective distribution coefficients. The experimental conditions of the present study are basically similar to but differ from those of SBMLC in the following respects:

(A) The ODSs used in this study contain larger amounts of residual silanol than those used in SBMLC;

(B) Samples are loaded up in larger amounts than in SBMLC; and

(C) The pressure in the present system (0.1 MPa) is significantly lower than that in SBMLC (2 MPa).

Not only the distribution term but the adsorption term is observed with regard to pyridine in the present study because of the above two factors (A) and (B). The saturated adsorption amount  $A_{\max}$  (expressed in terms of  $\mu\text{mol m}^{-2}$ ) is in the range of 5–29% of the residual silanol group estimated from  $SD_w$ . These support the fact that the adsorption term corresponds to the retention on the silica surface. The distribution term may, on the other hand, correspond to the retention on the alkyl-bonded layer and the retention on the alkyl-bonded layer/solvent interface.

The 50P retaining py under the varying conditions were re-equilibrated with water, for examining the reversibility of retention. In back-extraction when shaking  $V$  mL solution and  $m$  g ODS silica, if the adsorption is completely irreversible, only reagents ( $[R]'$ s,o) in the ODS phase retained by distribution are involved in mass transfer. The initial concentration of reagent  $C_0$  is given by Eq. (19).

$$C_0 = K_d[R] = [R]'\text{s,o} \quad (19)$$

Retention and mass balance of reagent are given by Eqs. (20) and (21), respectively.

$$[R]'\text{s} = K_d[R] \quad (20)$$

$$mC_0 = m[R]'\text{s} + V[R] \quad (21)$$

Substituting Eq. (21) for Eq. (20), concentration of reagent in aqueous phase is given by Eq. (22).

$$[R] = \frac{C_0}{K_d + V/m} \quad (22)$$

Since the adsorption is irreversible, the amount of reagent retained ( $[R]_s/\text{mol kg}^{-1}$ ) in ODS is calculated by Eq. (23).

$$[R]_s = \frac{K_{ad}A_{\max}[R]}{1 + K_{ad}[R]} + K_d[R] \quad (23)$$

The plot of py concentration in 50P against the aqueous py concentration given in Fig. 2 agreed well with the same retention isotherm as that given in Fig. 1(e); a slight upper deviation is attributed to the inevitable loss of ODS in the back-extraction process. In contrast, the calculated curve on the assumption of reversible distribution and irreversible adsorption is definitely higher than the experimental points. Although disappearance or tailing of peaks indicated some sort of irreversibility of retention in the time scale of RPLC,<sup>3-6</sup> retention was reversible in the time scale of SPE.

#### Properties of polymeric ODS silicas

Figure 3 shows the relationship between  $\log K_d'$  values of two nonpolar and one polar compound and  $SD_{\text{ODS}}$  values of polymeric ODS silicas (open symbols). The  $\log K_d'$  of each compound linearly decreased with an increase in  $SD_{\text{ODS}}$  in a substantially parallel manner. The difference in intercept between bz and tl (0.64) is comparable to the difference of their distribution constants between water and *n*-hexane (0.73). The properties of the ODS phase in ODS silicas are similar to those of common organic solvents. The decrease of  $\log K_d'$  value with an increase in  $SD_{\text{ODS}}$  suggests that reduction in the fraction of ODS functioning as the solvent is caused by the decreased wettability as demonstrated previously;<sup>7-9</sup> the ODS which is in

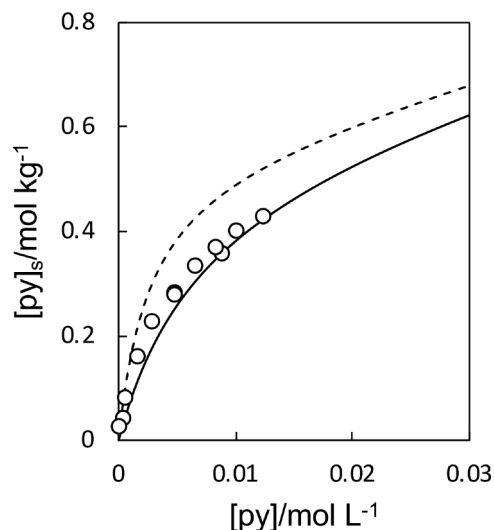


Fig. 2 Isotherm on back extraction of py from 50P to aqueous phase. Solid line: the same isotherm as that given in Fig. 1(e); broken line: calculated curve on the assumption of reversible distribution and irreversible adsorption.

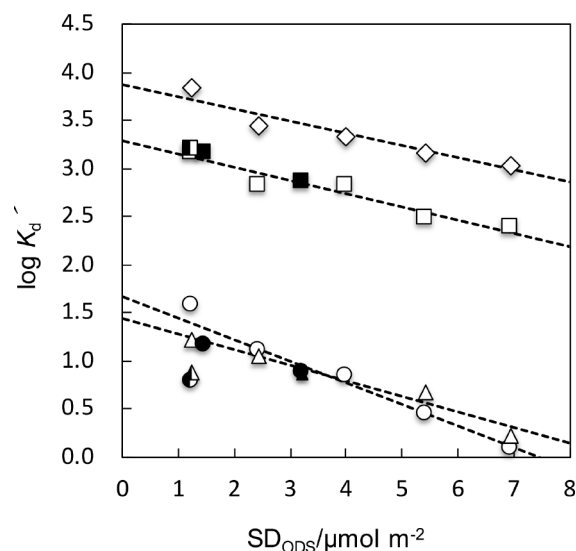


Fig. 3 Relation between  $\log K_d'$  of organic compounds and surface density of ODS group. Organic compound: bz ( $\square$ ), tl ( $\diamond$ ), py ( $\circ$ ), Hacac ( $\triangle$ ). Closed: 50M and 300M; half closed: 50PE, open: the others.

contact with a gas phase does not serve as the extracting medium. This was confirmed because under application of higher pressure by using an RPLC system, the retention of py on 300P was increased by 10 times (Fig. S4(e),  $0.27 \text{ mol kg}^{-1}$  at 7.8 MPa relative to  $0.03 \text{ mol kg}^{-1}$  at 0.1 MPa in equilibrium with  $[\text{py}] = 0.07 \text{ mol L}^{-1}$ ), while the retention on 50P remained approximately constant (Fig. 1(e),  $1.43 \text{ mol kg}^{-1}$  at 9.8 MPa relative to  $1.44 \text{ mol kg}^{-1}$  at 0.1 MPa in equilibrium with  $[\text{py}] = 0.15 \text{ mol L}^{-1}$ ). Provided that 100% ODS was effective in retention of py on 50P, the functioning ODS in 300P was only 3% at atmospheric pressure.

In the study of SBMLC, consistent results have been obtained based on the idea that the surface area of the alkyl-bonded layer/solvent interface is reduced while all the alkyl-bonded layers,

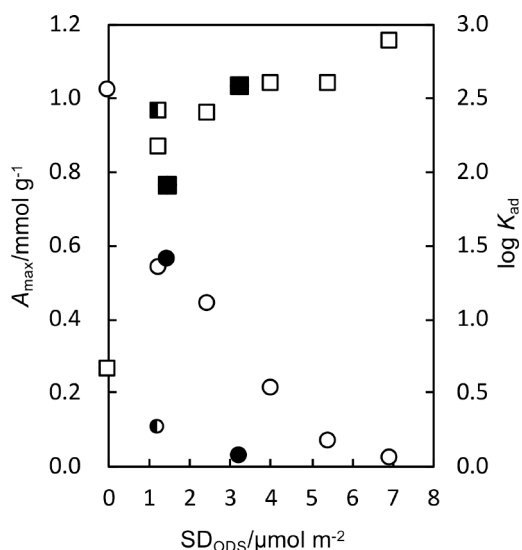


Fig. 4 Relation between  $A_{\max}$  or  $\log K_{\text{ad}}$  of py and surface density of ODS.  $A_{\max}$  (○);  $\log K_{\text{ad}}$  (□). Closed: 50 and 300M; half closed: 50PE, open: the others.

including the layer that is not exposed to the solvent but is exposed to the gas phase, serve as the stationary phase.<sup>16,19</sup> This suggests that a sample may rapidly arrive at the alkyl-bonded phase, to which the direct distribution is interfered with by the gas phase, by transfer in the lateral direction on the surface of the ODS particles. Although the reason for this striking difference from the present study is not clear at this stage, the pressure difference in the flow direction may enhance such a transfer in SBMLC (the difference (C) in the experimental conditions described above).

Figure 4 shows the relationship between  $A_{\max}$  or  $\log K_{\text{ad}}$  of py and  $\text{SD}_{\text{ODS}}$  of polymeric ODS silicas (open symbols; corresponding data for Hacac in Fig. S6 (Supporting Information)). The decrease in  $A_{\max}$  may be attributed to the reduction in fraction of the functioning ODS silica described above and to the reduction of the silanol group. In polymeric ODS silicas,  $\text{SD}_{\text{ODS}}$  may be increased not only by the reaction with silanol on base silica but by the reaction with introduced  $[\text{C}_{18}\text{H}_{37}\text{Si}(\text{OH})_2]$ -group, so that  $A_{\max}$  was moderately decreased with an increase in  $\text{SD}_{\text{ODS}}$ . In contrast, the  $\log K_{\text{ad}}$  value increased with an increase in  $\text{SD}_{\text{ODS}}$ . Since the strength of interaction of silanol with py is not intrinsically altered, this increase is attributed to the enhancement of hydrophobic interaction between py and the more densely introduced ODS group. Figure 4 also includes data relevant to 50S at abscissa equal to zero. Compared with the constants of ODS silicas, the  $A_{\max}$  value is much larger and the  $\log K_{\text{ad}}$  value is much smaller. The latter indicates that the higher aqueous py concentration (20–200 times) is required to achieve saturated adsorption.

Although the retention depends on these three parameters and cannot be simply expressed, 50P with  $\text{SD}_{\text{ODS}}$  of around  $1 \mu\text{mol m}^{-2}$  shows the maximum retention of the relatively low py concentration among ODS silicas and silicas examined in this study.

#### Properties of monomeric and endcapped polymeric ODS silicas

The corresponding data for the retention of py on monomeric (50 and 300M) and endcapped polymeric (50PE) ODS silicas are respectively shown by closed and half-closed symbols in Figs. 3 and 4. Both the  $\log K_{\text{ad}}$  values in Fig. 3 and the  $\log K_{\text{ad}}$

Table 3 Retention parameters of polar compounds from aqueous phase on 50P<sup>a,b</sup>

Reagent	$\log K_{\text{d}}$	$\log K_{\text{d}}'$	$A_{\max}$	$\log K_{\text{ad}}$	$\text{p}K_{\text{a}}^{29}$
py	0.79(2)	1.57(2)	0.54(2)	2.17(6)	5.24
lu	0.93(2)	1.71(2)	0.74(2)	2.76(5)	6.93
bpy	1.62(1)	2.40(1)	0.56(1)	3.30(1)	4.43

Reagent	$\log K_{\text{d}}$	$\log K_{\text{d}}'$	$A_{\max}$	$\log K_{\text{ad}}$	Charge (O) <sup>c</sup>
Hacac	0.44(1) <sup>d</sup>	1.22(1) <sup>d</sup>	0.42(3) <sup>d</sup>	1.93(2) <sup>d</sup>	−0.553
pt	0.91(1)	1.69(1)	0.35(3)	2.61(1)	−0.564
dca	0.48(2)	1.26(2)	n.s.	n.s.	−0.479
chx	0.66(1)	1.44(1)	0.46(1)	2.38(2)	−0.554
chd	0.54(2)	1.32(2)	0.63(3)	1.83(2)	−0.515

a. Error in the last digit shown in parentheses.

b. n.s.: negligibly small, n.m.: not measured.

c. Calculated by Gaussian 09; job type: optimization; method: ground state, HF, default spin; basic set: 3-21G.<sup>30</sup>

d. Cited from Ref. 25.

values in Fig. 4 of 50 and 300M are well accommodated in the correlation observed for polymeric ODSs; small trimethylsilyl group contributes neither to distribution nor to adsorption. The  $A_{\max}$  value of 50M is well accommodated in the correlation for polymeric ODSs in Fig. 4, while that of 300M is much lower than this correlation. In monomeric ODS,  $\text{SD}_{\text{ODS}}$  may be increased only at the sacrifice of silanol on base silica, so as to linearly reduce  $A_{\max}$ .

The  $\log K_{\text{d}}'$  values of py in retention on 50PE are appreciably smaller than those on 50P as shown in Fig. 3. When  $\text{SD}_{\text{ODS}} + \text{SD}_{\text{TMS}} = 3.17 \mu\text{mol m}^{-2}$  is taken as abscissa, better correlation is obtained. Reduction of silanol by TMS also reduces the fraction of the effectively functioning ODS phase. Similarly, the  $A_{\max}$  value in the retention of py on 50PE is reduced, compared with that on 50P.

#### Retention of other organic compounds

The retention isotherms of other related compounds on 50P are given in Fig. S7 (Supporting Information) and the relevant constants are summarized in Table 3. All the parameters in the retention of 2,6-lutidine are larger than those of pyridine, due to the higher lipophilicity and the higher basicity caused by the methyl groups at 2- and 6-positions; steric hindrance at these positions is not prevailing. The retention of bpy shows the comparable  $A_{\max}$  value and the much larger  $\log K_{\text{ad}}$  value, compared with that of py, in spite of the lower basicity. This indicates that two nitrogen atoms of bpy strongly interact with one silanol.

Among the oxygen-containing compounds, the electron density of the oxygen atom was calculated by Gaussian 09. In compounds with similar molecular structures (pt and Hacac, chx and chd), the electron densities were higher for ketones (pt, chx) than for the corresponding  $\beta$ -diketones (Hacac, chd),<sup>30</sup> due to the electron-withdrawing property of the second ketone group. Accordingly, between pt and Hacac, and chd and chx, the ketones show larger  $\log K_{\text{ad}}$  values than the  $\beta$ -diketones. Further reduction in electron density on oxygen of dca by two chloro substituents makes the adsorption term negligibly small.

These results show that adsorption of the nitrogen- or oxygen-compounds depend on the electron density of the donor atom. The number of silanol groups available for adsorption depends on the electron density of the donor atom and the three-dimensional structure of the compound, which determines the saturated adsorption amount.

## Conclusions

The performances of ODS silicas of varying properties were examined as the medium for batchwise SPE of organic compounds under atmospheric conditions. Nonpolar compounds were retained only by distribution, while polar compounds were retained by both distribution and adsorption; these were reversible in the time scale of SPE. An increase in  $SD_{\text{ODS}}$  reduces the fraction of effectively functioning ODS and the contribution of the distribution term. Under atmospheric pressure conditions, the densest ODS-introduced silica was able to utilize only 3% of the solid phase compared to the sparsest ODS-introduced silica. The increase in  $SD_{\text{ODS}}$  further reduces the  $A_{\text{max}}$  value, due to the reduction of the residual silanol group, and the reduction in the fraction of the functioning ODS, while increasing the adsorption constant, due to the enhanced hydrophobic interaction between organic compounds and ODS. The electron density of nitrogen or oxygen atom in the compound affects the adsorption to the residual silanol group. In summary, ODS silicas with appreciable amounts of silanol are superior for SPE at atmospheric pressure because of the relatively fast and reversible retention, the contribution of the adsorption term and the large fraction of functioning ODS without conditioning.

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## Supporting Information

Additional table and figures about the retention of other reagents on each ODS silica. This material is available free of charge on the Web at <http://www.jsac.or.jp/analsci/>.

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