Evaluation of adsorption of organic solvents to modified hydrophobic silica adsorbents based on Hansen solubility parameter

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ABSTRACT

Adsorption is an effective methodology for the removal of organic matter. Several studies have shown that adsorption performance is dependent on pore size, specific surface area, and the affinity between the adsorbent and adsorbed material. In this study, we concentrated on the effect of the affinity between the surface of the adsorbent and the adsorbed matter by examining the adsorption of organic solvents from organic/aqueous mixtures using three types of hydrophobic silica adsorbents. The Hansen solubility parameters (HSPs) of the adsorbents were determined using the group contribution method. A linear relationship between the logarithm of the amount of adsorbed organic solvent and the difference between the HSP values of the organic solvents and adsorbents was obtained with a high correlation coefficient. These experimental results suggest that the affinity between the adsorbent and adsorbed matter can be well-described by the HSPs of the components.

1. Introduction

Adsorption is a well-established and effective methodology for the removal of micro pollutants and is widely applied in wastewater treatment. Solid materials are used extensively as absorbents because of their large accessible surface areas and pore volumes and the possibility of regenerating the adsorbent at a later time [1,2].

However, adsorption isotherm is required for the adsorption process design. Time, cost, and toxicity may prevent the extensive collection of experimental adsorption data. Therefore, for the sake of preliminary design, a correlation capable of predicting adsorption equilibrium capacities from commonly available physicochemical properties of these compounds is highly needed [3].

Several studies have shown that adsorption is dependent on pore size, specific surface area, and the affinity between the adsorbent and adsorbed material [4–6]. However, there have been few quantitative reports that evaluate the effect of affinity on adsorption. Thus, it is necessary to numerically verify the effects of affinity.

The linear solvation energy relationship (LSER) model has been proposed as an affinity (interaction) evaluation method in adsorption [3,7].

The LSER model takes into account the hydrogen bonding or dipole-dipole force as an interaction. Zhang et al. reported adaptation to solid-liquid adsorption of LSER model [3]. However, it is difficult to determine the parameters. It is thought that it is necessary to propose more simple indicators.

To elucidate the mechanisms by which affinity affects adsorption, we focused on the Hansen solubility parameters (HSPs) of various materials [8].

The Hildebrand solubility parameter (δt) [9,10] is commonly used to evaluate the cohesion energies of substances. The solubility parameter, a physical property representing the cohesion energy density of a substance, is useful for evaluating the compatibility, wettability, and cohesiveness or dispersibility of substances. Hansen further defined the Hildebrand solubility parameter as comprising three components based on the type of molecular interaction involved: namely, dispersion forces (δ_d), intermolecular dipole interactions (δ_p), and hydrogen-bonding interactions (δ_h).

Sato et al. evaluated the correlation between oxygen solubility in pure organic solvents and R_a, i.e., the 3D-HSP distance between oxygen and the solvent [12].

Moreover, good correlation between R_a and solubility was observed for the HSPs of oxygen.

In the present study, for adsorbents with constant specific surface area and pore diameter, we investigated changes in the adsorption performance related to the adsorbent affinity. We performed adsorption experiments using silica with different functional groups to test the effect of the affinity between the adsorbent and organic solvent and to clarify the effect of the surface functional groups on the adsorption amount.

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Nomenclature

E	cohesive energy, J/mol
E_d	cohesive energy of dispersion interaction, J/mol
E_p	cohesive energy of dipole interaction, J/mol
E_h	cohesive energy of hydrogen-bonding interaction, J/mol
V	volume of solvent, L
δ_t	solubility parameter, MPa$^{1/2}$
δ_d	Hansen solubility parameter of dispersion interaction, MPa$^{1/2}$
δ_p	Hansen solubility parameter of dipole interaction, MPa$^{1/2}$
δ_p	Hansen solubility parameter of hydrogen-bonding

	interaction, MPa$^{1/2}$
R_a	distance between Hansen solubility parameters, MPa$^{1/2}$
φ	volume ratio, −
R	correlation coefficient, −
q	adsorbed amount, mmol/g
C	concentration of solvents, mol/L
W	weight of adsorbent, g
V_M	molar volume, cm^3/mol
F_{di}	Dispersion component of molar attraction function, J$^{1/2}$ cm$^{3/2}$/mol
F_{pi}	Polar component of molar attraction function, J$^{1/2}$ cm$^{3/2}$/mol

Araki et al. reported that the flux of an organic compound through a membrane is related to the difference between the HSPs of the membrane and organic compound [6]. In other words, the affinity between the organic compounds and membrane is the dominant factor in membrane separation.

Using this approach, we established the HSPs of the adsorbent and found a correlation between R_a and the amount of solvent adsorbed, similar to the correlation previously reported for oxygen [12].

2. Experimental section

2.1. Theory of Hansen solubility parameter

The solubility parameter δ_t [(MPa)$^{1/2}$] used in the solubility evaluation was defined as

$$\delta_t = \left(\frac{\Delta E^V}{V_M}\right)^{1/2} \tag{1}$$

where ΔE is the liquid cohesion energy [J] and VM is the molar volume [cm^3/mol] [9].

Hansen divided the cohesion energy ΔE [J] of the Hildebrand solubility parameter into three components (i.e., dispersion interactions Ed [J/mol], dipole interactions Ep [J/mol], and hydrogen-bonding interaction Eh [J/mol]), which can be expressed as follows: [13]

$$\Delta E^V = \Delta E_d^V + \Delta E_p^V + \Delta E_h^V \tag{2}$$

$$\delta_d = \left(\frac{\Delta E_d^V}{V_M}\right)^{1/2}, \ \delta_p = \left(\frac{\Delta E_p^V}{V_M}\right)^{1/2}, \ \delta_h = \left(\frac{\Delta E_h^V}{V_M}\right)^{1/2} \tag{3}$$

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \tag{4}$$

Here, δ_d [(MPa)$^{1/2}$], δ_p [(MPa)$^{1/2}$], and δ_h [(MPa)$^{1/2}$] represent the dispersion force factor, dipole interaction force factor, and hydrogen-bonding force factor of the HSP, respectively. Quantitative evaluation of the solubility can be represented by the value of R_a [(MPa)$^{1/2}$], which reflects the distance of the HSPs of both substances:

$$R_a = [4 \cdot (\delta_{d,1} - \delta_{d,2})^2 + (\delta_{p,1} - \delta_{p,2})^2 + (\delta_{h,1} - \delta_{h,2})^2]^{1/2} \tag{5}$$

A smaller R_a means a higher solubility of each substance because the interaction forces acting between the molecules are similar. Thus, substances with large R_a values exhibit low solubility.

The solubility parameter of a mixed solvent is calculated using the following equation:

$$\delta_i = \varphi_1 \delta_{i,1} + \varphi_2 \delta_{i,2} \tag{6}$$

where φ is the volume fraction of each of the mixed solvents, with the subscripts 1 and 2 representing components 1 and 2, respectively. The subscript i can be d, p, or h (representing the dispersion interaction, dipole interaction, or hydrogen-bonding interaction factors, respectively).

2.2. Calculation of HSPs of adsorbents

We calculated the HSPs of hydrophobic silica samples (modified with different functional groups) using the Hoftyzer–van Krevelen group contribution method [14]. The following equations were used to estimate the HSPs:

$$\delta_d = \frac{\sum F_{di}}{V_M} \tag{7}$$

$$\delta_p = \frac{\sqrt{\sum F_{pi}^2}}{V_M} \tag{8}$$

$$\delta_h = \sqrt{\frac{\sum E_{hi}}{V_M}} \tag{9}$$

where δ_d is the dispersion HSP, δ_p is the polar HSP, δ_h is the hydrogen-bonding HSP, v is the molar volume, F_{di} is the group contribution of the dispersion component of structural group i, F_{pi} is the group contribution of the polar component, and E_{hi} is the hydrogen-bonding energy. If two identical polar groups are present in a symmetrical position, the value of δ_p calculated using Eq. (8) must be multiplied by a symmetry factor of 0.5, 0.25, or 0 for one, two, or more-than-two planes of symmetry, respectively. For molecules with several planes of symmetry, $\delta_h = 0$. The molar volume was estimated using Hoy's method [6,14].

In addition, the HSP value of a polymer with a molecular structure consisting of repetition of a basic structure, such as the hydrophobic silica adsorbent used in this research, can be estimated using the group contribution method for one segment of the structure [6].

The HSPs of the adsorbents were calculated from the amounts of organic solvent adsorbed from organic/aqueous mixtures. The detailed procedure for the calculation of the HSPs of the adsorbents was as follows. First, the amounts adsorbed from the organic/aqueous mixtures with known HSPs were measured. Second, we assumed that the HSP values of the adsorbents, R_a could be calculated from the HSP values of the adsorbents and solvents. The correlation coefficient between R_a and the logarithm of the amount of solvent adsorbed was calculated. Finally, the HSPs of the adsorbents were determined.

2.3. Preparation of hydrophobic silica sol adsorbents

To prepare the phenyltrimethoxysilane (PhTMS) sol adsorbent, a PhTMS silica sol was first prepared by hydrolysis and copolymerization of PhTMS (0.1 mol) in the presence of cetyltrimethylammonium bromide (CTAB) (0.008 mol) in 25 mL of ethanol with gentle stirring. This concentration of CTAB was higher than the critical micelle concentration of CTAB in ethanol (0.24 mol mL^{-1}) [6]. The hydrolysis and condensation reactions of the PhTMS silica sol were promoted by adding 7.5 mL of 1 mol L^{-1} HNO$_3$ dropwise to the mixture. Then, the mixture was stirred continuously at room temperature for 3 h. Next, 3 mL of the mixture was extracted, placed on a square alumina plate, and calcined at 453 K for 3 h. The adsorbents were then washed with ethanol to

remove CTAB. Ethyltrimethoxysilane (EtTMS)- and propyltrimethoxysilane (PrTMS)-modified sol adsorbents were also prepared using the same method with 3 h of stirring after addition of the HNO$_3$ solution.

In order to check whether the hydrophobic functional group was introduced on the surface of the silica adsorbent, analysis was carried out using FT-IR (FT/IR-6800, JASCO).

2.4. Experimental method

We prepared eight types of 5 wt% organic-water solutions (100 mL). Silica sol adsorbent (0.2 g) was added to the mixed solvents (40 mL). The mixed solvent and silica were stirred together at room temperature for 24 h, and the silica was removed using a 0.2-μm filter [15]. The density before and after adsorption in the mixed solvent was measured using a density meter (Anton paar DMA4500M).

A calibration curve of density and concentration in various water-organic mixed solutions was prepared. Using the prepared calibration curve, the concentration was obtained from the density of the mixed solvent before and after adsorption and the adsorption amount was calculated.

The adsorbed amount was calculated based on the concentration before and after adsorption of the mixed solvents using the following equation: [15]

$$q = \frac{(C_0 - C)V}{W} \tag{10}$$

In addition, in order to ascertain the time to reach saturation in various adsorbents, time-dependent adsorption experiments up to 24 h were conducted. As a result, it was confirmed that sufficient saturation adsorption was reached in each adsorbent and each mixed solution in 24 h.

3. Results and discussion

3.1. Characterization of silica adsorbents

The FT-IR spectra of the ethyl-, propyl-, and phenyl-modified adsorbents are shown in Fig. 1. The peak at 1020 and 1065 cm^{-1} appearing in all adsorbents are the peaks corresponding to an asymmetric vibration of Si−O−Si [16,17]. The C−H stretching vibration of benzene derivatives generally appear in the region 3000–3100 cm^{-1}, which is the characteristic region for ready identification of C−H stretching vibration [18]. The C−H symmetric stretching vibration are observed at 3000–3100 cm^{-1} in the experimental FT-IR spectrum of PhTMS-modified adsorbent.

The adsorption bands for C−C stretching modes are occurring in the range of 1200–1650 cm^{-1} for aromatic compounds [18].

The peak at 1250 cm^{-1} in ETMS-modified adsorbent is can be ascribed to the Si-C2H5 vibration [19].

Also, the peaks at 2800–3000 cm^{-1} found in ETMS- and PrTMS-modified adsorbents is the peak corresponding to saturated aliphatic hydrocarbons [19,20]. Furthermore the peak at 1403 cm^{-1} referring to the H−C−H bending vibration [19,20]. From the above results, it was confirmed that the desired hydrophobic functional group could be introduced.

3.2. Calculated HSPs of adsorbents using group contribution method

The siloxane network was formed in each membrane, as shown in Fig. 2, when the hydrolysis and condensation reactions were completed. The HSP of a single unit of each silica adsorbent (n = 1, Fig. 2) was calculated using the Hoftyzer–van Krevelen group contribution method.

The HSPs of the hydrophobic silica sol adsorbents determined using the group contribution method are listed in Table 1. To estimate the number of hydrophobic silica units with each functional group, F$_d$, F$_p$, and E$_h$ of siloxane (≡Si−O−) were calculated using least-squares

regression analysis with the HSP values of TEOS, octamethylcyclotetrasiloxane and decamethylcyclopentasiloxane, which were obtained from the software Hansen Solubility Parameters in Practice.

The HSPs of the adsorbents modified by the ethyl and propyl functional groups were almost the same; however, the HSPs of the phenyl-modified adsorbents showed differences. The δ_d parameter of the phenyl-modified adsorbent was larger than that of the others.

δ_d is connected to polarizability (and therefore to refractive index) [13]. Cyclic compounds such as Benzene and Toluene can be mentioned for the reason that the polarizability is high. This is because the electrons derived from an aromatic is affecting [13]. Therefore, it is considered that δd of PhTMS adsorbent substituted by cyclic structure was higher than δd of other adsorbents.

Because δ_d tends to increase as the molecular size increases, the hydrophobic silica adsorbent used in this study also appeared to show the same tendency. As the carbon number of the hydrophobic functional group attached to Si increased, the polarity was decreased, and the values of δ_p and δ_h tended to be lower. This tendency appears to originate from the effect of polarity on one molecule decreasing as the number of carbons increases. This tendency is the same as that reported for the HSP of alcohols [13].

3.3. Adsorbed amounts of organic solvents from organic aqueous mixtures

Adsorption by the hydrophobic silica adsorbents for eight organic/aqueous mixtures was measured at 298.2 K.

The results of the adsorption experiments on the ethyl-, propyl-, and phenyl-modified adsorbents are presented in Table 2. To confirm whether factors other than affinity affected the adsorption, we focused on the molecular diameter. The molecular diameters of the solvents and the adsorption amounts in the adsorbents modified with propyl groups are provided in Table 3 and Fig. 3.

The results confirmed that there was a difference in the adsorption amount in the solvents with the same molecular diameter. In addition, in the solvent used this time, the adsorption amount of methyl acetate with the largest molecular diameter was maximized. From the above results, it is considered that the adsorption mechanism in the hydrophobic silica adsorbent used in this study does not have a substantial effect on the adsorption amount due to the molecular and pore diameters.
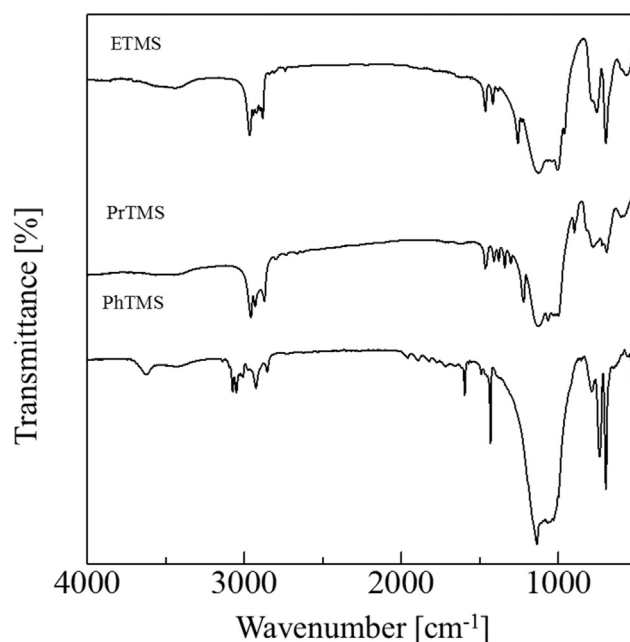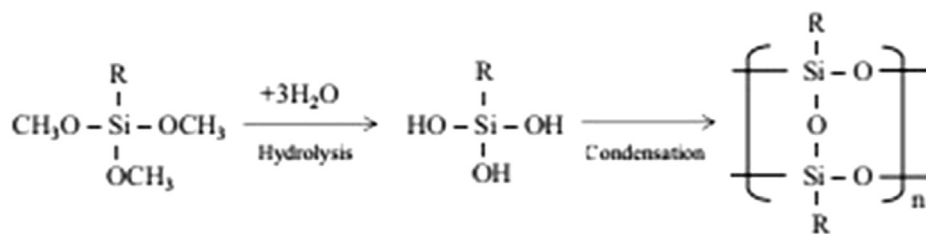

Fig. 1. FT-IR spectra of hydrophobic silica adsorbents.

R= ethyl, n-propyl, phenyl group

Fig. 2. Schematic of the reaction process for silicon alkoxide.

Table 1
HSPs of different types of hydrophobic silica.

functional group	δ_d [(MPa)$^{1/2}$]	δ_p [(MPa)$^{1/2}$]	δ_h [(MPa)$^{1/2}$]	δ_t [(MPa)$^{1/2}$]
$-CH_2CH_3$	14.4	4.4	5.1	15.9
$-CH_2CH_2CH_3$	14.9	3.5	4.6	16.0
⟨phenyl⟩	19.7	3.3	4.4	20.5

Table 3
Kinetic diameter of solvent and adsorbed amount by Propyl adsorbent.

Solvent	Kinetic diameter [nm]	q [mmol/g]	Log q [–]
Ethyl acetate	0.52	5.57	−2.25
Methyl acetate	0.50	4.19	−2.38
THF	–	3.51	−2.45
MEK	0.50	2.88	−2.54
Acetone	0.47	2.39	−2.62
1-Butanol	0.50	1.09	−2.96
2-Propanol	0.47	1.40	−2.85
1-Propanol	0.47	1.27	−2.90

To investigate the effect of affinity, attention was paid to the difference R_a between the HSP value of each adsorbent and that of the solvent. The HSP value of the solvent, the HSP difference R_a between each adsorbent and solvent, and the logarithm of the adsorption amount are listed in Table 4.

The relationship between R_a and the logarithm of the adsorption amount is shown in Fig. 4. A linear relationship was observed between R_a and the logarithm of the adsorption amount. As a result, the adsorption amount increased as R_a decreased. The correlation coefficients of the ethyl-, propyl-, and phenyl-modified adsorbents were calculated, and very high correlation was confirmed, with R = 0.924, 0.956, and 0.981, respectively.

Based on these results, the affinity of the adsorbent and target substance was considered to be dominant in adsorption, and the following expressions were obtained:

$$\text{Log } q = -0.1292 \cdot R_a - 1.8784 \tag{11}$$

$$\text{Log } q = -0.0668 \cdot R_a - 2.0772 \tag{12}$$

$$\text{Log } q = -0.1385 \cdot R_a - 1.082 \tag{13}$$

The amounts of organic solvent adsorption by each adsorbent and those calculated from the HSPs for the eight solvents are shown in Tables 5–7. The average difference between the measured and calculated values of the ethyl-, propyl-, and phenyl-modified silica adsorbents were 9.13%, 2.08%, and 2.33%, respectively, and the maximum deviations were 22.33%, 3.59%, and 6.56%, respectively. Furthermore, the correlation coefficients between the measured and calculated adsorbed amounts of each adsorbent were 0.961, 0.968, and
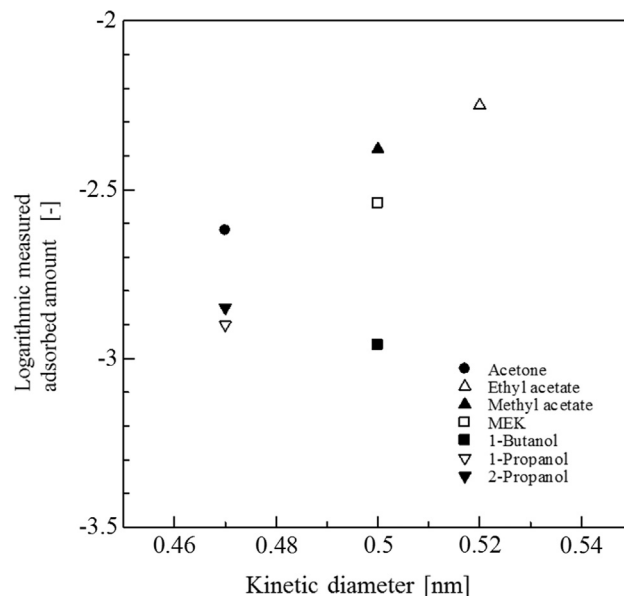

Fig. 3. Correlation between adsorbed amounts and kinetic diameter of molecules with propyl hydrophobic silica membrane.

0.980, respectively.

Next, we investigated whether it was possible to estimate the

Table 2
Adsorbed amount of each hydrophobic adsorbents.

Solvent	Ethyl		Propyl		Phenyl	
	q [mmol/g]	Log q [–]	q [mmol/g]	Log q [–]	q [mmol/g]	Log q [–]
Ethyl acetate	6.18	−2.21	5.57	−2.25	5.44	−2.26
Methyl acetate	2.78	−2.56	4.19	−2.38	5.19	−2.28
Tetrahydrofuran (THF)	3.37	−2.47	3.51	−2.45	7.1	−2.15
Methyl ethyl ketone (MEK)	1.68	−2.77	2.88	−2.54	4.07	−2.39
Acetone	1.60	−2.80	2.39	−2.62	2.32	−2.63
1-Butanol	1.11	−2.96	1.09	−2.96	0.85	−3.07
2-Propanol	0.27	−3.58	1.40	−2.85	0.66	−3.18
1-Propanol	0.22	−3.65	1.27	−2.90	0.75	−3.12

Table 4

HSPs of solvents and amounts of solvent adsorbed to ethyl-, propyl- and phenyl- modified silica.

| Solvent	δ_d [(MPa)$^{1/2}$]	δ_p [(MPa)$^{1/2}$]	δ_h [(MPa)$^{1/2}$]	R_a(ethyl-) [(MPa)$^{1/2}$]	Log q (ethyl-) [-]	R_a (propyl-) [(MPa)$^{1/2}$]	Log q (propyl-) [–]	R_a (phenyl-) [(MPa)$^{1/2}$]	Log q (phenyl-) [–]
Acetone	15.5	10.4	7.0	6.7	−2.80	7.5	−2.62	11.3	−2.63
Ethyl acetate	15.8	5.3	7.2	3.6	−2.21	3.7	−2.25	8.5	−2.26
Methyl Acetate	15.5	7.2	7.6	4.3	−2.56	5.0	−2.38	9.8	−2.28
THF	16.8	5.7	8.0	5.7	−2.47	5.6	−2.45	7.2	−2.15
MEK	16.0	9.0	5.1	5.6	−2.77	6.0	−2.54	9.3	−2.39
1-Butanol	16.0	5.7	15.8	11.2	−2.96	11.7	−2.96	13.8	−3.07
1-Propanol	16.0	6.8	17.4	12.9	−3.65	13.5	−2.90	15.4	−3.12
2-Propanol	15.8	6.1	16.4	11.7	−3.58	12.3	−2.85	14.6	−3.18
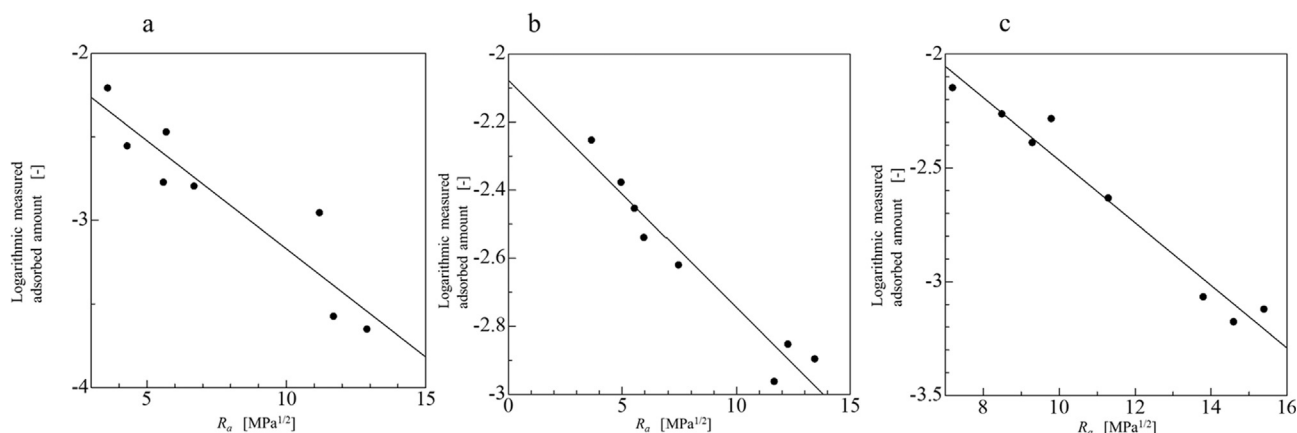
Fig. 4. Relationship between the separation of HSPs of solvent/modified adsorbent, calculated by the group contribution method, and adsorbed amounts of organic solvents a: ethyl, b: propyl, c: phenyl.

Table 5

HSPs of solvents and amounts adsorbed to ethyl-modified silica.

	R_a [(MPa)$^{1/2}$]	log q calculated	log q measured	Deviation [%]
Acetone	6.7	−2.74	−2.62	4.47
Ethyl acetate	3.6	−2.34	−2.25	3.76
Methyl acetate	4.3	−2.44	−2.38	2.44
THF	5.7	−2.62	−2.45	6.56
MEK	5.6	−2.60	−2.54	2.39
1-Butanol	11.2	−3.32	−2.96	12.21
1-Propanol	12.9	−3.54	−2.90	22.33
2-Propanol	11.7	−3.39	−2.85	18.90

Table 7

HSPs of solvents and amounts adsorbed to phenyl-modified silica.

	R_a [(MPa)$^{1/2}$]	log q calculated	log q measured	Deviation [%]
Acetone	11.3	−2.64	−2.63	0.32
Ethyl acetate	8.5	−2.26	−2.26	0.23
Methyl acetate	9.8	−2.43	−2.28	6.56
THF	7.2	−2.08	−2.15	3.17
MEK	9.3	−2.37	−2.39	0.67
1-Butanol	13.8	−2.99	−3.07	2.48
1-Propanol	15.4	−3.21	−3.12	2.75
2-Propanol	14.6	−3.10	−3.18	2.43

Table 6

HSPs of solvents and amounts adsorbed to propyl-modified silica.

	R_a [(MPa)$^{1/2}$]	log q calculated	log q measured	Deviation [%]
Acetone	7.5	−2.58	−2.62	1.73
Ethyl acetate	3.7	−2.32	−2.25	3.04
Methyl acetate	5.0	−2.41	−2.38	1.31
THF	5.6	−2.45	−2.45	0.23
MEK	6.0	−2.48	−2.54	2.51
1-Butanol	11.7	−2.86	−2.96	3.59
1-Propanol	13.5	−2.98	−2.90	2.73
2-Propanol	12.3	−2.90	−2.85	1.52

adsorption amount without the need for experiments using the relational expression of the R_a adsorption amount. Dimethyl formamide (DMF) was selected as the solvent for this investigation. Experiments were performed using the ethyl-modified adsorbent. The HSPs of DMF were $\delta_d = 17.4$, $\delta_p = 13.7$, and $\delta_h = 11.3$, and $R_a = 12.7$ with the ethyl-modified adsorbent. Log q = −3.59 when the adsorption amount was estimated using equation (11). The measured value of the

adsorption amount of DMF was log q = −3.56, and the deviation was 1.09%. Based on these results, it is considered possible to estimate the adsorption amount from the HSP value of the adsorbent and the HSP difference R_a of the adsorbate.

3.4. Calculation of HSPs of adsorbents

A high correlation between the adsorption amount and R_a was confirmed. Sato et al. reported that it is possible to estimate the gas HSP using the gas solubility and HSP difference R_a between the solute gas and solvent [12] because the gas solubility strongly depends on the affinity between the gas and solvent. In this study, we observed that the affinity of adsorbents and adsorbates is dominant in adsorption. Therefore, we determined the HSP of the adsorbent using a correlation similar to that for gas solubility. The HSPs of the adsorbents were calculated from the amount of solvent adsorbed from the eight organic solvents. The HSPs of the adsorbents were calculated to achieve the highest correlation coefficient of log q (logarithm of the adsorbed amount of each organic solvent) and R_a. The correlation coefficient between the logarithm of the adsorbed amount of each hydrophobic

Table 8
The difference in HSP value of each adsorption in each calculation method.

functional group	δ_d [(MPa) $^{1/2}$]	δ_p [(MPa) $^{1/2}$]	δ_h [(MPa) $^{1/2}$]	δ_t [(MPa) $^{1/2}$]	R_a [(MPa) $^{1/2}$]
Ethyl (Group contribution method)	14.4	4.4	5.1	15.9	–
Ethyl (estimated value)	14.5	0.0	4.7	15.2	4.4
Propyl (Group contribution method)	14.9	3.5	4.6	16.0	–
Propyl (estimated value)	15.6	5.3	7.1	18.0	3.4
Phenyl (Group contribution method)	19.7	3.3	4.4	20.5	–
Phenyl (estimated value)	16.8	6.0	6.7	19.1	6.7

silica adsorbent modified with EtTMS, PrTMS, or PhTMS and the R_a value calculated from the HSP values of the adsorbents and solvents were Rethyl = 0.951, Rpropyl = 0.991, and Rphenyl = 0.978.

The HSP values for each silica adsorbent determined from the correlation between the adsorption amount and R_a are listed in Table 8.

Here, R_a represents the difference in HSP between the HSP value and the estimated value obtained using the group contribution method.

The R_a values between the estimated values for the ethyl- and propyl-modified adsorbents and the values obtained using the group contribution method were 4.4 or less. However, R_a for the phenyl-modified adsorbent was 6.7. The HSP estimated from the adsorption amount is a value that conforms to the actual measurement result. The value of δ_d of the solvent studied this time was investigated in the range of 15–17. It is considered that the HSP value of the adsorbate substituted with Phenyl group differs from the result by the group contribution method. It is considered that a more reliable value can be obtained by conducting investigations using a solvent having a δ_d range of 18 or more. Considering the results of the precision experiment of the formula using DMF, it is possible to estimate adsorption amount by using HSP theory.

It is considered that the change in the adsorption amount in the same adsorbent is determined by the affinity between the adsorbent surface and the adsorbate.

4. Conclusion

The HSPs of hydrophobic silica sol adsorbents were determined using the group contribution method. We measured the amounts of organic solvents adsorbed to hydrophobic silica adsorbents for organic/aqueous mixtures. The correlation coefficients between the logarithm of the amount of solvent adsorbed and the R_a values were calculated based on the HSP values of the adsorbent and solvents. Adsorption to ethyl-, propyl-, and phenyl-modified adsorbents from organic/aqueous mixtures produced correlations of 0.924, 0.967, and 0.981, respectively. We calculated the HSP of each adsorbent based on the correlation between R_a and the amounts of solvent adsorbed. Our experimental results suggest that the affinity between the adsorbent and adsorbed matter can be well described by the HSPs.

Acknowledgment

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.seppur.2018.08.034.

References

[1] T.J. Bandosz, Activated Carbon Surfaces in Environmental Remediation PREFACE, Elsevier Academic Press Inc, San Diego, 2006, pp. V–VI.
[2] P.M. Schoenecker, C.G. Carson, H. Jasuja, C.J.J. Flemming, K.S. Walton, Effect of water adsorption on retention of structure and surface area of metal-organic frameworks, Ind. Eng. Chem. Res. 51 (18) (2012) 6513–6519.
[3] S.J. Zhang, X.T. Liu, T. Karanfil, Applicability of the linear solvation energy relationships in the prediction for adsorption of aromatic compounds on activated carbons from aqueous solutions, Sep. Purif. Technol. 117 (2013) 111–117.
[4] H. Marsh, F. RodriguezReinoso, Activated carbon, Activated Carbon (2006) 1–536.
[5] C. Moreno-Castilla, Adsorption of organic solutes from dilute aqueous solutions, in: E.J. Bottani, J.M.D. Tascon (Eds.), Adsorption by Carbons, Elsevier Science Bv, Amsterdam, 2008, pp. 653–678.
[6] S. Araki, D. Gondo, S. Imasaka, H. Yamamoto, Permeation properties of organic compounds from aqueous solutions through hydrophobic silica membranes with different functional groups by pervaporation, J. Membr. Sci. 514 (2016) 458–466.
[7] M.J. Kamlet, R.M. Doherty, M.H. Abraham, R.W. Taft, Linear solvation energy relationships. 33. An analysis of the factors that influence adsorption of organic compounds on activated carbon, Carbon 23 (1985) 549–554.
[8] C.M. Hansen, A.L. Smith, Using Hansen solubility parameters to correlate solubility of C-60 fullerene in organic solvents and in polymers, Carbon 42 (8–9) (2004) 1591–1597.
[9] J.H. Hildebrand, R.L. Scott, Regular Solutions, Prentice-Hall, Englewood Cliffs, 1962.
[10] J.H. Hildebrand, R.L. Scott, The Solubility of Nonelectrolytes, 3rd ed., Dover Publications Inc., New York, 1950.
[12] T. Sato, Y. Hamada, M. Sumikawa, S. Araki, H. Yamamoto, Solubility of oxygen in organic solvents and calculation of the hansen solubility parameters of oxygen, Ind. Eng. Chem. Res. 53 (49) (2014) 19331–19337.
[13] C.M. Hansen, Hansen Solubility Parameters: A User's Handbook, CRC Press, Boca Raton, FL, 1999.
[14] D.W. van Krevelen, et al., Properties of Polymers, 4th ed., Elsevier, 2009.
[15] B.Z. Li, Z.P. Lei, X.H. Zhang, Z.G. Huang, Adsorption of simple aromatics from aqueous solutions on modified activated carbon fibers, Catal. Today 158 (3–4) (2010) 515–520.
[16] C.Y. Wang, J.Z. Zheng, Z.X. Shen, Y. Lin, A.T.S. Wee, Elimination Of O-2 plasma damage of low-k methyl silsesquioxane film by As implantation, Thin Solid Films 397 (2001) 90–94.
[17] S. Yasuhara, J. Chung, K. Tajima, H. Yano, S. Kadomura, M. Yoshimaru, N. Matsunaga, S. Samukawa, Impact of film structure on damage to low-k SiOCH film during plasma exposure, J. Phys. D-Appl. Phys. 42 (23) (2009) 8.
[18] Z. Demircioglu, F.A. Ozdemir, O. Dayan, Z. Serbetci, N. Ozdemir, Synthesis, X-ray diffraction method, spectroscopic characterization (FT-IR, H-1 and C-13 NMR), antimicrobial activity, Hirshfeld surface analysis and DFT computations of novel sulfonamide derivatives, J. Mol. Struct. 1161 (2018) 122–137.
[19] J. Yang, J.R. Chen, J.H. Song, Studies of the surface wettability and hydrothermal stability of methyl-modified silica films by FT-IR and Raman spectra, Vib. Spectrosc. 50 (2) (2009) 178–184.
[20] H. Yoshida, A. Ehara, H. Matsuura, Density functional vibrational analysis using wavenumber-linear scale factors, Chem. Phys. Lett. 325 (4) (2000) 477–483.