Adsorption of Sodium Dodecylbenzene Sulfonate on Highly Humic Non-allophanic Andisol at High-Electrolyte Concentration

Farook AHMED[1], Munehide ISHIGURO[2], Kazuki MORIGUCHI[1][†] and Takeo AKAE[1]

Abstract : To clarify the adsorption characteristics of surfactants, it is important to understand the surfactant behavior in the soil and water environments. However, there are few adsorption studies for highly humic soil. In this study, the adsorption characteristics of dodecylbenzene sulfonates in a highly humic soil were investigated. A non-allophanic Andisol was used since this soil contains a large amount of humic substances and is only negatively charged. Thus, electrically, only repulsive force is generated between the soil and the surfactant. The adsorption amount was measured using the batch method at an electrolyte concentration of 100 mmol L^{-1} NaCl in order to shield the electric field near the soil particle surface and emphasize hydrophobic reactions. The adsorption isotherm was examined using the Langmuir-Freundlich-Hill equation. The adsorbed amount increased sharply with increasing concentrations in the low-concentration range. The sharp increase indicated cooperative adsorption caused by hydrophobic interaction among the carbon chains of adsorbing surfactants. The adsorption amount became higher at a lower pH because electrostatic repulsion between the soil and the surfactant decreased. The adsorption of dodecylbenzene sulfonate with a linear carbon chain was larger than that with a branched chain due to the difference of the carbon chain structure.
Key words : anionic surfactant, electrostatic repulsive force, dodecylbenzene sulfonate (DBS), adsorption isotherm, volcanic ash soil.

1. Introduction

Sodium dodecylbenzene sulfonates (SDBS) are very common, efficient anionic surfactants (Fachini et al., 2007) as active ingredients of laundry detergent and many domestic and industrial materials including chemical fertilizers as an anti-caking agent. It is also used in agricultural chemicals as an emulsifying agent, because of its ability to change the physicochemical nature of surfaces (Koopal et al., 1999). Linear alkylbenzene sulfonate (LAS), one of the major constituents of synthetic detergent, is the most widely used SDBS for domestic and industrial purposes, in both percentage and absolute amount (Inoue et al., 1978; He et al., 1991). It is also the most common pollutant found in almost all environmental settings (Sullivan and Swisher, 1969; McEvoy and Giger, 1986; Takada and Ishiwatari, 1987; Yediler et al., 1989; Papaport and Eckhoff, 1990; McAvoy et al., 1993). LAS is the most widely used anionic surfactant in detergent formulations and surface cleaners (Marcomini and Giger, 1988). Overall, SDBSs are used in large quantities and enter the environment primarily through waste water and sludge.

When these compounds are adsorbed in soils, they appear to degrade slowly (Tabor and Barber, 1996) and to impede microbial processes in soil (Kristiansen et al., 2003). Adsorption of LAS by soils and sediments is an important process affecting its transport, and toxicity (Wolf and Feijtel, 1998; Knabel et al., 1996; Fleld et al., 1992; Garcia et al., 2005; Rubio et al., 1996) and, thus, its application in remediation of contaminated soil and groundwater (West and Harwell, 1992; Rouse and Sabatini, 1993; Ko et al., 1998a; DiVincenzo and Dentel, 1996; Allred and Brown, 1996). The adsorption of LAS may also affect the environmental behavior of the toxic substances (Jones-Hughes and Turner, 2005; Ko et al., 1998a; DiVincenzo and Dentel, 1996) and nanoparticles (Lacoanet et al., 2004). In past decades, adsorption studies have been conducted to understand the fate of discharged LAS (Wolf and Feijtel, 1998). Since the surfactant concentrations used in soil and groundwater remediation (Zhao et al., 2006; SDBS concentration from 0.2 to 10 g L^{-1}) and nanomaterial preparation are always higher than critical micelle concentrations (CMCs) (West and Harwell,

[1]Graduate School of Environmental Science, Okayama University, Okayama 700-8530, Japan
[2]Research Faculty of Agriculture, Hokkaido University, Sapporo 060-8589, Japan
Corresponding author : F. AHMED, Graduate School of Environmental Science, Okayama University, 3-1-1 Tsushima-naka, Okayama 700-8530, Japan. E-mail: farookahmed12@yahoo.com
Tel. & Fax 086-251-8874.
Present address : [†]Kinki Regional Development Bureau, Ministry of Land, Infrastructure and Transport, 1-5-44, Otemae, Chuo-ku, Osaka 540-8586, Japan

Table 1. Physical and chemical characteristics of the soil used in the experiment.

Soil Name	Sand	Silt	Clay	Texture	pH	Carbon content	[a]CEC	[b]AEC
	(%)					(%)	(mmol$_c$ kg^{-1})	
Andisol	43.6	31.8	24.6	Clay loam	[c]5.0, [d]4.2	13.8	12.3	0

[a]CEC was measured at pH 6 with a 1 mmol$_c$ L^{-1} KNO$_3$ solution.

[b]AEC was measured at pH 6 with a 1 mmol$_c$ L^{-1} K$_2$SO$_4$ solution.

[c]pH was measured with distilled water (soil : distilled water at the ratio of 1 : 5)

[d]pH was measured with 0.1M KCl (soil : 0.1M KCl at the ratio of 1 : 2.5)

1992; Tanaka et al., 1997; Ko et al., 1998b; Lecoanet et al., 2004), adsorption of LAS in a wide concentration range needs to be investigated. Different mechanisms such as hydrophobic adsorption (Hand and Williams, 1987; Di Toro et al., 1990; Westall et al., 1999), specific adsorption (Ou et al., 1996; Westall et al., 1999), hydrogen bonding (Ou et al., 1996), electrostatic interactions (Westall et al., 1999) and precipitation (West and Harwell, 1992; Rouse and Sabatini, 1993) have been suggested as determining the adsorption of LAS on soils, but there is no consensus on this issue. The influence of sediment on adsorption of LAS has been reviewed by Wolf and Feijtel (1998). As different soil and sediment constituents may have different adsorption characteristics (Knaebel et al., 1994), adsorption of LAS would depend not only on the types of these constituents but also on their relative contents (Zhu et al., 2003; Wolf and Feijtel, 1998).

Branched-carbon-chain DBS has low bio-degradability (Alexander M 1973; Cain RB 1987; Cain RB 1994; Greek BF 1991). In some Latin American countries, branched-chain SDBSs in different formulations are used due to their low cost, to the detriment of the environment and especially water quality (Campos-Garcia et al., 1999). Few studies exist about branched-chain DBS adsorption on soils. Adsorption studies comparing linear and branched-carbon-chain structures are also rare.

In this study, the adsorption characteristics of DBS in a highly humic soil were investigated in the surfactant concentration range from very low to around critical micelle concentration by using an anionic surfactant selective electrode that we ourselves devised and built. A non-allophanic Andisol was used because the soil contains a large amount of humic substances and is only negatively charged (Ishiguro et al., 2003). The adsorption amount was measured using a batch method at an electrolyte concentration of 100 mmol L^{-1} NaCl in order to shield the electric field near the soil surface and emphasize hydrophobic interaction. The adsorption isotherm was evaluated using the Langmuir–Freundlich–Hill equation. The influences of carbon chain structure on adsorption were also evaluated.

2. Materials and methods

2. 1 Soil

Highly humic, non-allophanic Andisol (volcanic ash soil) of A horizon from Daisen grazing ground, Tottori Prefecture, Japan was used in this experiment. The physical and chemical characteristics of the soil are given in Table 1. Moist field soil sieved with a 2-mm sieve was used in the experiment.

2. 2 Surfactants

Anionic surfactants, SDBS, with branched and linear carbon chains having the same chemical composition (C$_{12}$H$_{25}$C$_6$H$_4$SO$_3$Na) and molecular weight of 348.48 g mol^{-1} were purchased from Tokyo Kasei Kogyo Co. The two types of SDBS had purities of about 95% and were used without further purification. The former mixture of hydrophobic branched chains consisted of 12 carbon molecules. The branched structures were not constant, but their structures were not linear. The latter contained hydrophobic 12-carbon linear-chain molecules.

2. 3 Adsorption experiment

A batch experiment was conducted to obtain the DBS adsorption isotherm of the soil. The experiment was conducted to investigate the influence of pH, time, and carbon chain structure at room temperature (25 ± 1℃). The soil (2.5 g dry weight basis) was placed in a 50-cm^3 centrifuge tube. It was equilibrated with a 100 mmol L^{-1} NaCl solution, and the solution pH was adjusted to 4.5, 5.5 or 6.5 by adding dilute HCl or NaOH. After discarding the supernatant from the tube, 25 ml of SDBS solution (ranging from 0.0008 to 10.0 mmol L^{-1}) at 100 mmol L^{-1} NaCl was mixed in the soil and shaken well for 3 or 24 hours. After the elapsed time the soil solution was centrifuged for 10
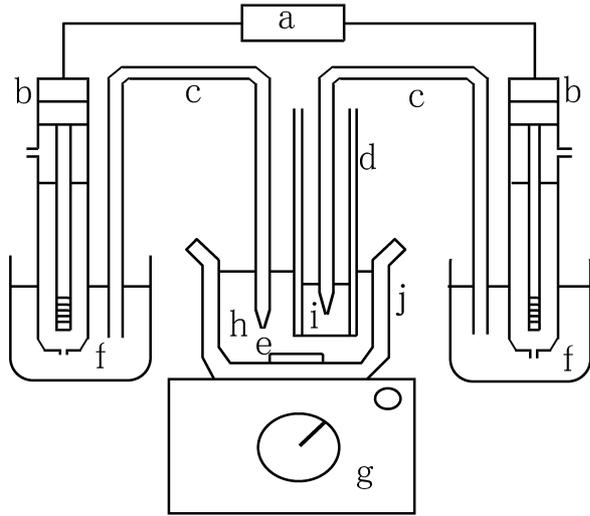
Fig. 1 The schematic diagram of the anionic surfactant selective electrode used in the experiment. a : Electrometer (Advantest R8240), b : AgCl/Ag electrode (DKK,TOA HS-305D), c：NH$_4$NO$_3$（Agar bridge）, d：Ion selective electrode, e：Magnet, f：1M NH$_4$NO$_3$, g : Stirrer, h : Measured/test solution, i : Reference solution, j : Beaker.

min at 8000 rpm. The supernatant of the tube was collected and the surfactant concentration was measured by an anionic surfactant selective electrode（Fukui et al., 2003）that we ourselves devised and built. The concentration cell was constructed as follows:

Ag/AgCl electrode｜Agar bridge｜reference solution （C_0）｜functional membrane｜test solution（C_1）｜Agar bridge｜Ag/AgCl electrode,

where C_0 and C_1 are the concentrations of the surfactant in the reference solution and that in the collected supernatant. The schematic diagrams of the anionic surfactant selective electrode used in the experiment are given in Fig. 1.

The electromotive force（EMF）was read using a digital voltmeter with high input impedance at 25 ± 1℃. The EMF, E, can be expressed with the following equation:

$$E = S \log (C_1/C_0), \tag{1}$$

where S is the experimental slope. The theoretical value of S is 59.2 mV at 25℃（Nernstian slope）. The measured values for the standard solutions ranged from 54.35 mV to 59.00 mV. When the concentration was higher than the critical micelle concentration, the concentration was measured after dilution. The electrolyte concentrations for the standard solutions, test solutions and reference solutions were all 100 mmol L^{-1} NaCl. Because humic substances dissolved in the solution affect the measurement when the electrode is dipped longer in the solution without washing, the electrode

was carefully washed before each measurement and always checked with standard solution in order to get the proper result.

The adsorbed amount of surfactant in the soil was obtained using the following equation,

DBS adsorption（mmol kg^{-1}）=｛added DBS conc.（mmol L^{-1}）×0.025（L）− DBS conc. in supernatant（mmol L^{-1}）×（0.025+V）(L)｝/Dry weight of the soil（kg）, (2)

where V（L）is the water volume remaining in the soil after discarding the supernatant and before adding the SDBS solution. The experiment was conducted under the 100 mmol L^{-1} NaCl solution condition, in order to decrease the influence of the negative charge of the soil.

2. 4 Critical micelle concentration（CMC）

SDBS CMC at 100 mmol L^{-1} NaCl was obtained using the anionic surfactant selective electrode. The EMF was measured at each SDBS concentration. Under the CMC, a straight calibration line（EMF versus the logarithm of the SDBS concentration）was obtained according to equation（1）. Above the CMC, the EMF became almost constant. The CMC was obtained at the kink of the calibration line（Ishiguro et al., 2007; Ishiguro and Koopal, 2009）.

2. 5 Theoretical analysis of adsorption isotherm

To evaluate the adsorption isotherm, the following equation was used:

$$q = Q \frac{(KC)^n}{1 + (KC)^n} \tag{3}$$

$$\Delta G = RT \log K, \tag{4}$$

where q is the adsorption amount, Q is the maximum adsorption amount, C is the equilibrium concentration （mol L^{-1}）, K is the adsorption constant, n is non-ideality （deviation from Langmuir equation, n=1）, ΔG is the difference in free energy before and after adsorption （J mol^{-1}）, R is the gas constant and T is the absolute temperature. Equation（3）can be re-written as follows（Ooi et al., 2000）:

$$\frac{\theta}{1 - \theta} = (KC)^n, \tag{5}$$

where θ is q/Q. When θ is ≪ 1, the equation（5）can be re-written as follows:

$$\log q = n\log C + \log (QK^n). \tag{6}$$

Therefore, when the isotherm is plotted in double loga-

rithmic scale, the slope indicates the n value for q$\ll$$Q$.

When n is larger than unity, this equation is called the Hill equation (Hill, 1910; Ooi et al., 2000); implying that adsorbates attract each other and adsorb cooperatively. The cooperativity occurs when adsorbed molecules attract each other by lateral interaction; adsorption becomes stronger with that lateral interaction. When n is smaller than unity, this equation is called the Langmuir–Freundlich equation (Jaroniec, 1983, Ooi et al., 2000); this indicates heterogeneity of adsorbing sites. For surfactant adsorption on the soil both the heterogeneity of the adsorbing sites on the soil and a positive cooperativity ($n > 1$) due to hydrophobic attraction will play a role. To express this, eq. (3) is called the Langmuir–Freundlich–Hill (LFH) equation, and n can be smaller or larger than unity. The LFH eq. with $n < 1$ implies that the heterogeneity effects are larger than the hydrophobic effects, and $n > 1$ implies that the hydrophobic attraction is stronger than the heterogeneity effects. Pseudo–ideality ($n = 1$) occurs when the effects of heterogeneity and hydrophobicity compensate each other (Ishiguro and Koopal, 2011).
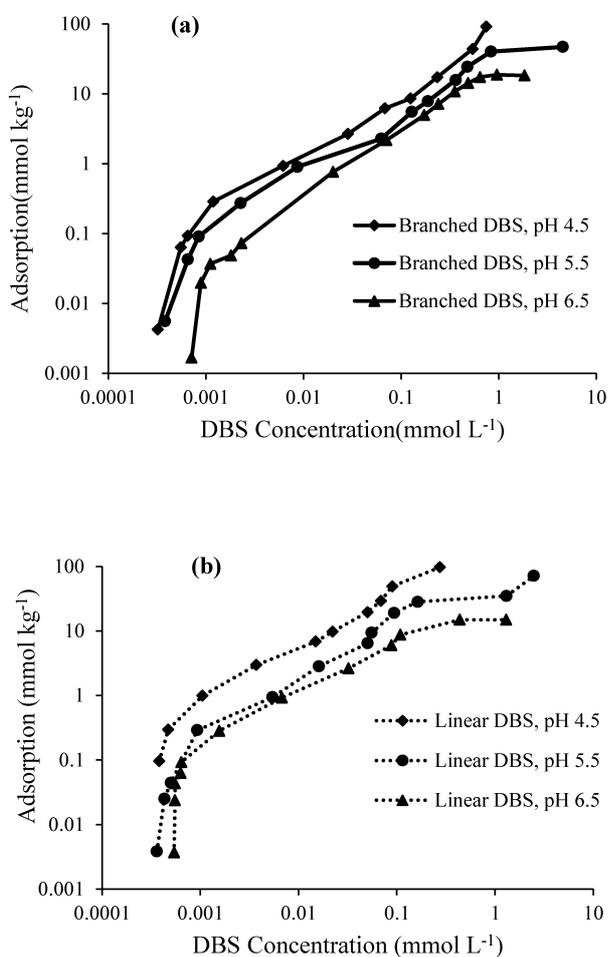
3. Results and Discussion

3. 1 Effect of pH on DBS adsorption

The adsorption isotherms for branched–carbon–chain DBS and linear–carbon–chain DBS are shown in Fig. 2. The DBS concentrations for the adsorption isotherms in the figures show the solution concentrations in the supernatants after mixing and centrifugation. The highest adsorption was observed at pH 4.5 and the lowest at pH 6.5 for both branched and linear DBS in this experiment (Fig. 2). This result clearly shows that adsorption is higher at a lower pH and lower at a higher pH. The electrostatic force is repulsive because both DBS and the soil are negatively charged and no positive charge was detected by AEC measurement (Ishiguro et al., 2003). Therefore, the electrostatic interaction lowers the adsorption. When the soil pH increases, the negative pH–dependent charge of the soil increases, and the increased electrostatic repulsive force causes the adsorption to decrease. A similar trend was reported by Fytianos et al. (1998) in soil of different organic matter content. Our result shows that pH has a strong influence on the adsorption isotherm.
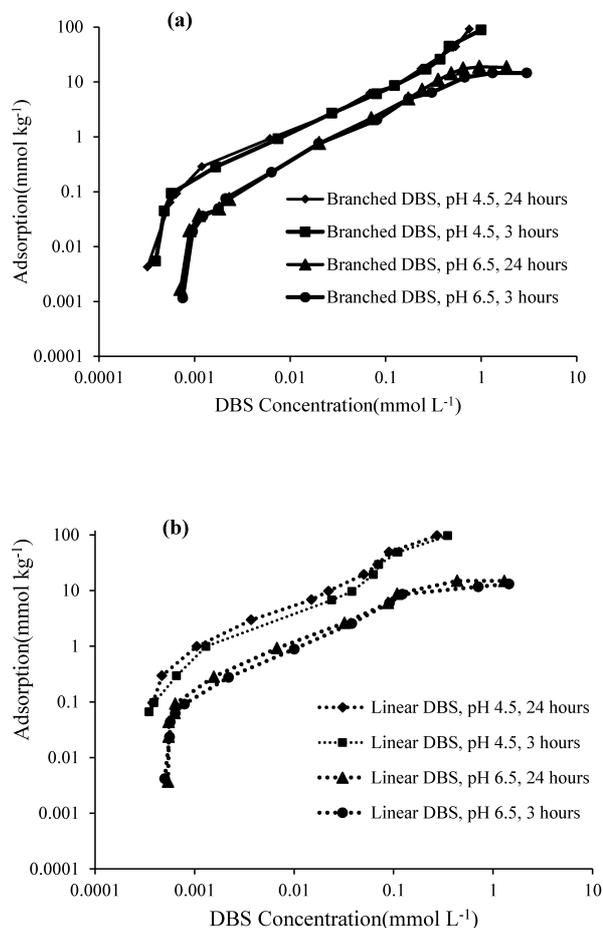

Fig. 2 Effect of pH on (a) branched DBS and (b) linear DBS adsorption isotherm. (after 24-hour mixing)

Fig. 3 Adsorption isotherm of DBS at different time (a) branched DBS and (b) linear DBS (after 3-and 24-hour mixing).

Because both DBS and the soil have hydrophobic parts and the electrostatic interaction is repulsive, DBS is mainly adsorbed by hydrophobic interactions.

3. 2 Effect of time on DBS adsorption

The adsorption isotherms after 3–hour and 24–hour mixing are compared in Fig. 3. No significant difference was detected at all pH conditions. This result indicates that the soil is equilibrated within 3 hours. Li et al. (2008) reported that DBS required 100 minutes for adsorption equilibrium in marine sediments. For linear–carbon–chain DBS, the adsorptions after 24 hours were slightly larger than those after 3 hours. This result indicates the influence of DBS decomposition, because linear–carbon–chain DBS decomposes more readily than branched–carbon–chain DBS when it is dissolved in water (Sekiguchi et al., 1975). As the adsorption amount was calculated with the subtraction

equation (2), the decomposed amount is included in the adsorption amount. However, because the difference between those after 3 hours and 24 hours was not significant, the adsorbed linear–carbon–chain DBS decomposes slowly, as Tabor and Barber (1996) suggested. Further experimental research is needed to identify the restrictive effect of adsorption on the decomposition.

3. 3 Evaluation of the adsorption isotherms

The experimental result showed that the adsorption of DBS on the soil increases with the increment of concentration for both branched and linear DBS irrespective of pH (Figs. 2 and 3). At much lower concentrations of DBS ($<0.001\,\mathrm{mmol\,L^{-1}}$) the adsorption isotherms were very steep, indicating strong cooperativity ($n \gg 1$); the surfactant molecules aggregate due to hydrophobic interaction among their carbon chains and are adsorbed
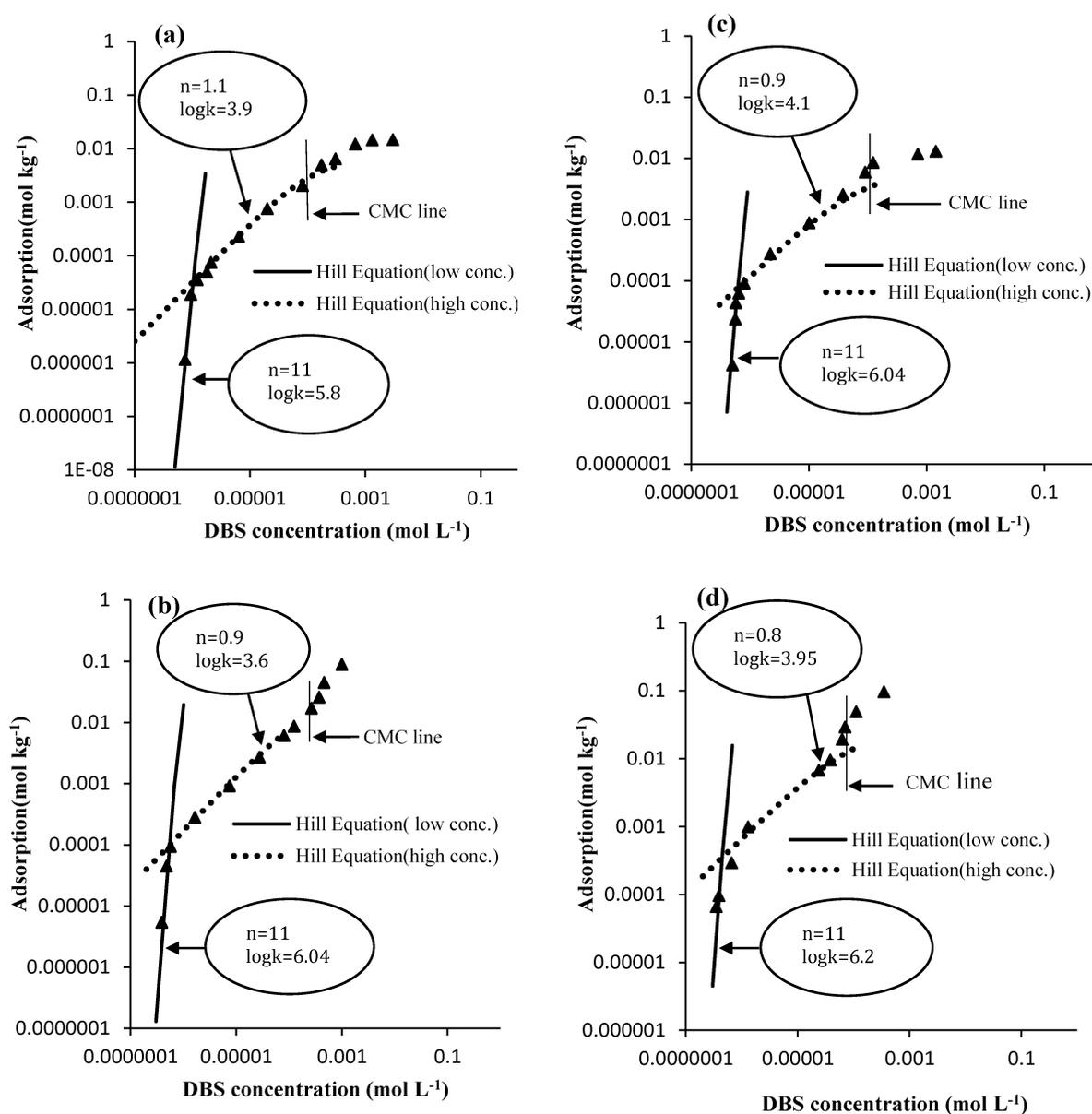

Fig. 4 Comparison of the calculated adsorption values using the Hill equation (3) and measured adsorption isotherm. (a) Branched DBS at pH 6.5, (b) branched DBS at pH 4.5, (c) linear DBS at pH 6.5 and (d) linear DBS at pH 4.5.

Table 2. Obtained *n* value and *K* value by using Hill equation (3) for branched and linear DBS.

pH		pH 4.5		pH 6.5	
Concentration		Low	High	Low	High
n	Branched	11	0.9	11	1.1
	Linear	11	0.8	11	0.9
log *K*	Branched	6.04	3.6	5.78	3.9
	Linear	6.2	3.95	6.04	4.1

on the soil surface together. Above these lower concentrations, the adsorption isotherms show a gradual increase to around CMC (0.33 mmol L^{-1} and 0.09 mmol L^{-1} for branched and linear DBS, respectively). The electrostatic repulsive force between the soil and the surfactant is supposed to decrease the slope of the isotherm. The surfactant adsorption leads to an increase in the negative charge. This affects the adsorption and contributes to the decrease of the slope of the isotherm.

The adsorption equation (3) is applied to the adsorption isotherms as shown in Fig. 4. The adsorption isotherms are plotted on a log–log scale in order to distinguish the isotherms. The *n* value in equation (3) is equal to the slope of the isotherm in the log–log scale as explained by equation (6). The obtained *n* values and *K* values by fitting with the obtained data are listed in Table 2. Curve–fitting calculations were conducted at two regions separately for each adsorption isotherm: a region at lower concentration and that at a higher concentration around the CMC. The *n* values are larger at lower concentrations, indicating strong cooperative adsorption as mentioned before. At pH 4.5 for linear DBS, the adsorption amounts at very low concentrations corresponding to strong cooperative adsorption could not be measured because the adsorption increased at too low a concentration. Therefore, the calculated isotherm at pH 4.5 at lower concentration for linear DBS was given by using *n*=11 as shown in Figure 4 (d). The *n* value denotes the number of aggregated surfactant molecules when adsorbed onto one surface site (Hayakawa and Kwak, 1991; Ooi et al., 2000).

The *n* values at higher concentrations around the CMC show roughly 1.0 for all conditions. The *n* = 1 indicates no cooperativity. In this region, cooperative adsorption caused by the carbon chains is cancelled with the electrostatic repulsive force between the surfac-

tant and the soil surface. DBS is adsorbed separately on each remaining adsorption site of the soil by hydrophobic interaction.

The steep increase is followed by a gradual increase in all adsorption isotherms. Similar isotherms have been observed for a cationic surfactant–anionic polymer system (Satake and Yang, 1976; Shirahama, 1998; Ishiguro and Koopal, 2009). In their cases, the adsorbing force between the surfactant and polymer was due to electrostatic interactions. In our study, the electrostatic force was repulsive, different from their conditions. The cooperative interaction was generated by the carbon chains of the surfactants, and the gradual increase of the isotherm at higher concentration is related to the electrostatic repulsion caused by the charge of adsorbed surfactant in both systems. Cooperative adsorption has been observed also in an anionic surfactant–neutral polymer system (Arai et al., 1971; Shirahama, 1974). On the other hand, in an anionic surfactant–humic acid system, distinct adsorption was not observed (Koopal et al., 2004; Yee et al., 2009). The high adsorption on the soil indicates that part of humic substances in the soil are much more hydrophobic than humic acids.

3. 4 Comparison between branched and linear DBS adsorption isotherms

From the experimental results it was observed that the linear DBS adsorption is higher than that of branched DBS adsorption in the soil in all pH conditions (Fig 5). The results indicate that the linear DBS adsorbs and aggregates together at a lower concentration compared to the branched DBS. That is confirmed by the fact that the CMC of the linear SDBS was lower than the branched SDBS. The former was 0.09 mmol L^{-1} while the latter was 0.33 mmol L^{-1}, measured by the anionic surfactant selective electrode. The conformation of linear DBS is more advantageous for aggregation on the soil and micellization in water than

that of branched DBS.

4. Conclusions

The adsorption characteristics of DBS on a highly humic non-allophanic Andisol were systematically investigated. The adsorption was measured using the batch method at the electrolyte concentration of 100 mmol L^{-1} NaCl. The adsorption isotherm was evaluated using the Langmuir-Freundlich-Hill equation.

The adsorption amount on the soil increased sharply with increasing concentrations at lower concentrations for both the branched and linear DBS. The sharp increase indicates cooperative adsorption caused by hydrophobic interaction among the carbon chains of adsorbing surfactants. This cooperative adsorption phenomenon is a novel observation for soils. This finding and other characteristics could be detected because (i) the electric potential near the soil surface was shielded by the high electrolyte concentration, (ii) a highly humic soil with many hydrophobic sites was used, and (iii) a highly sensitive method of surfactant-selective electrode measurement was applied. The obtained adsorption characteristics can be fundamentally applied to any soil containing humic substances although those adsorption amounts would be smaller than our results.

The adsorption amount decreased with increasing pH because electrostatic repulsion increased at higher pH. Because the adsorption is strongly affected by pH, the pH must be carefully considered when the fate of ionic surfactants in soils is discussed.

The adsorption of linear-carbon-chain DBS was larger than that of branched-carbon-chain due to the difference of the chain structure. There was no significant difference in adsorption amounts after 3 and 24 hours; hence, the reaction must reach equilibrium within 3 hours while decomposition is not significant or small within 24 hours. Purification of water contaminated with SDBS by highly humic non-allophanic Andisol will therefore take more than 24 hours. In perspective, further research is needed on the decomposition of the surfactant.

Acknowledgements

List of Abbreviations

SDBS : sodium dodecylbenzene sulfonate
CMC : critical micelle concentration
EMF : electromotive force
LAS : linear alkylbenzene sulfonate
CEC : cation exchange capacity
AEC : anion exchange capacity

References

Alexander, M. (1973) : Nonbiodegradable and other recalcitrant molecules. Biotechnol Bioeng., 15 : 611-647.

Allred, B. and Brown, G. O. (1996) : Anionic surfactant transport characteristics in unsaturated soil. Soil Sci., 161 : 415-425.

Arai, H., Murata, M. and Shinoda, K. (1971) : The interaction between polymer and surfactant : The composition of the complex between polyvinylpyrrolidone and sodium alkyl sulfate as revealed by surface tension, dialysis, and solubilization. J. Colloid Interface Sci., 37 : 223-227.

Buffle, J. (1988) : Complexation reactions in aquatic systems, Ellis Horwood Ltd., Chichester.

Cain, R. B. (1987) : Boidegradation of anionic surfactants. Biochem. Soc. Trans., 15 : 7-22.

Cain, R. B. (1994) : Boidegradation of detergents. Curr. Opin. Biotechnol., 5 : 266-274.

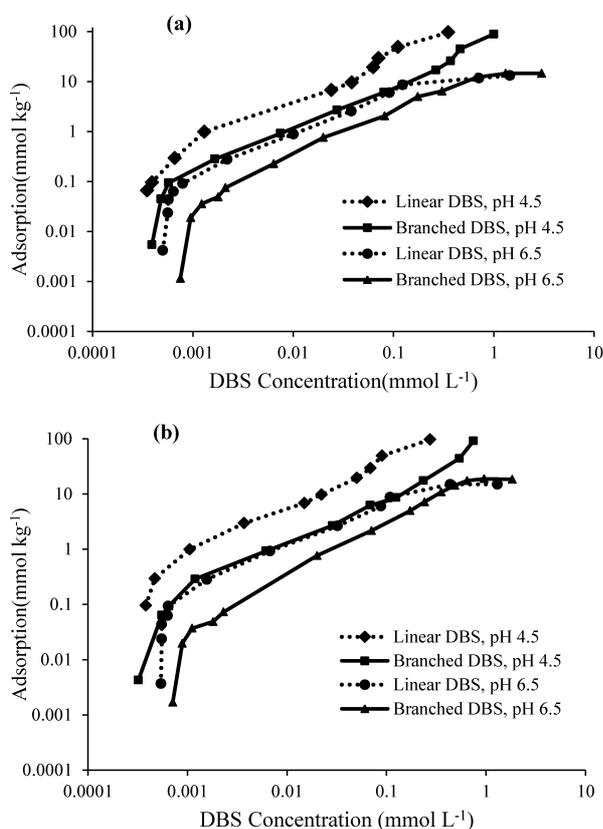Campos-Garcia, J., Esteve, A., Vazquez-Duhalt, R., Ramos, J. L. and Soberon-Chavez, G. (1999) : The Branched-Chain Do-

Fig. 5 Comparison between branched and linear DBS adsorption at pH 4.5 and 6.5 (a) after 3-hour and (b) 24-hour mixing.

decylbenzene Sulfonate Degradation Pathway of Pseudomonas aeruginosa W51D Involves a Novel Route for Degradation of the Surfactant Lateral Alkyl Chain. Applied and Environmental Microbiology, 65 : 3730-3734.

Di Toro, D. M., Dodge, L. J. and Hand, V. C. (1990) : A model for anionic surfactant sorption. Environ. Sci. Technol., 24 : 1013-1020.

DiVincenzo, J. P. and Dentel, S. K. (1996) : Sorption-desorption of 1,2,4-trichlorobenzene on soil : anionic surfactant and cationic polyelectrolyte effects. J. Environ. Qual., 25 : 1193-1202.

Fachini, A., Mendes, M. A., Joekes, I. and Eberlin, M. N. (2007) : Oxidation of Sodium Dodecylbenzenesulfonate with Chrysotile : On-line Monitoring by Membrane Introduction Mass Spectrometry. J. Suffact Deterg., 10 : 207-210.

Fleld, J. A., Barber II, L. B., Thurman, E. M., Moore, B. L., Lawrence, D. L. and Peakee, D. A. (1992) : Fate of alkylbenzene sulfonates and dialkyltetralinsulfonates in sewage contaminated groundwater. Environ. Sci. Technol., 26 : 1140-1148.

Fukui, H., Kaminaga, A., Maeda, T. and Hayakawa, K. (2003) : Preparation of surfactant anion-selective electrodes with different selectivity coefficients and a trial to determine each component in binary surfactant mixtures. Analytica Chimica Acta, 481 : 221-228.

Fytianos, K., Voudrias, E. and Papamichali, A. (1998) : Behavior and fate of linear alkylbenzene sulfonate in different soils. Chemosphere, 36 : 2741-2746.

Garcia, M. T., Campos, E., Ribosa, I., Latorre, A. and Sanchez-Leal, J. (2005) : Anaerobic digestion of linear alkylbenzene sulfonates : biodegradation kinetics and metabolite analysis. Chemosphere, 60 : 1636-1643.

Greek, B. F. (1991) : Sales of detergents growing despite recession. Chem. Eng. News., 69 : 25-52.

Hand, V. C. and Williams, G. K. (1987) : Structure activity relationship for sorption of linear alkyl benzene sulphonates. Environ. Sci. Technol., 21 : 370-373.

Hayakawa, K. and Kwak. J. C. T. (1991) : Interactions between polymers and cationic surfactants. *In* Cationic surfactants, Eds DN Rubingh and PM Holland, pp.189-248. Marcel Dekker, New York.

He, W.S., Wang, R. F., Zhang, C. F. and Chen, J. J.(1991): Erythrocyte micronucleus of tadpole (Bufobufo andrewsi) by synthetic detergent powder. Acta Scientiae Curcumstantiae, 11 (3) : 351-357

Hill, A. V. (1910) : A new mathematical treatment of changes of ionic concentration in muscle and nerve under the action of electric currents, with a theory as to their mode of excitation. J Physiol., 40 : 190-224.

Inoue, K., Kaneko, K. and Yoshida, M. (1978) : Adsorption of dodecyl-benzenesulphonates by soil colloids and influence of soil colloids on their degradation. Soil Sci. Plant Nutr.,

24 : 91-102.

Ishiguro, M., Manabe, Y., Seo, S. and Akae, T. (2003) : Nitrate transport in volcanic ash soil of A and B horizons affected by sulfate, Soil Sci. Plant Nutr., 49 : 249-254.

Ishiguro, M., Tan, W. and Koopal, L. K. (2007) : Binding of cationic surfactants to humic substances. Colloids and Surfaces A, 306 : 29-39

Ishiguro, M. and Koopal, L. K. (2009) : Binding of alkylpyridinium chloride surfactants to sodium polystyrene sulfonate. Colloids and Surfaces A, 347 : 69-75

Ishiguro, M. and Koopal, L. K. (2011) : Predictive model of cationic surfactant binding to humic substances. Colloids and Surfaces A, 379 : 70-78.

Jaroniec, M. (1983) : Physical adsorption on heterogeneous solids. Adv. Colloid Interface Sci., 18 : 149-225.

Jones-Hughes, T. and Turner, A. (2005) : Sorption of ionic surfactants to estuarine sediment and their influence on the sequestration of phenanthrene. Environ. Sci. Technol., 39 : 1688-1697.

Knabel, D. B., Federle, T. F., McAvoy, D. C. and Vestal, J. R. (1996) : Microbial mineralization of organic compounds in an acidic agricultural soil : effects of preadsorption to various soil constituents. Environ. Toxicol. Chem., 15 : 1865-1875.

Knaebel, D. B., Federle, T. F., McAvoy, D. C. and Vestal, J. R. (1994) : The effect of mineral and organic soil constituents on the microbial mineralization of organic compounds in a natural soil. Appl. Environ. Microbiol., 60 : 4500-4508.

Ko, S. O., Schlautman, M. A. and Carraway, E. R. (1998a) : Partitioning of hydrophobic organic compounds to sorbed surfactants. 1. Experimental studies. Environ. Sci. Technol., 32 : 2769-2775.

Ko, S. O., Schlautman, M. A. and Carraway, E. R. (1998b) : Effects of solution chemistry on the partitioning of phenanthrene to sorbed surfactants. Environ. Sci. Technol., 32 : 3542-3548.

Koopal, L. K., Goloub, T., Keizer, A. D. and Sidorova, M. P. (1999) : The effect of cationic surfactants on wetting, colloid stability and flotation of silica. Colloids and Surfaces A, 151 : 15-25.

Koopal, L. K., Goloub, T. and Davis, A. (2004) : Binding of ionic surfactants to purified humic acid. J. Colloid Interf. Sci., 275 : 360-367.

Kristiansen, I. B., Jonge, H. D., Nornberg, P., Mather-Christensen, O. and Elsgaard, L. (2003) : Sorption of linear alkylbenzene sulfonate to soil components and effects on microbial iron reduction. Environ. Texicol. Chem., 22 : 1221-1228.

Lecoanet, H. F., Bottero, J. Y. and Wiesner, M. R. (2004) : Laboratory assessment of the mobility of nanomaterials in porous media. Environ. Sci. Technol., 38 : 5164-5169.

Li, X. X., Yang, G. and Cao, X. (2008) : Sorption behaviors of so-

dium dodecylbenzene sulfonate（SDBS）on marine sediments. Water Air Soil Pollut., 194：23–30.

Marcomini, A. and Giger, W.（1988）：Behaviour of LAS in sewage treatment. Tenside Surf. Det., 25：226–229.

McAvoy, D. C., Eckhoff, W. S. and Papaport, R. A.（1993）：Fate of linear alkylbenzene sulfonate in the environment. Environ. Toxic. Chem., 12：977–987.

McEvoy, J. and Giger, W.（1986）：Determination of linear alkylbenzenesulfonates in sewage sludge by high–resolution gas chromatography/mass spectrometry. Environ. Sci. Technol., 20：376–383.

Ooi, S., Adachi, Y., Haraguchi, N. and Koopal, L. K.（2000）：Fundamentals and applications of soil colloid science, Development of theoretical treatment of adsorption. J. Japanese Soc. Irrigation, Drainage and Reclamation Engng., 68：479–486（in Japanese）.

Ou, Z. Q., Yediler, A., He, Y. W., Jia, L. Q., Kettrup, A. and Sun, T. H.（1996）：Adsorption of linear alkylbenzene sulfonate（LAS）on soils. Chemosphere, 32：827–839.

Papaport, R. A., and Eckhoff, W. S.（1990）：Monitoring linear alkylbenzene sulfonate in the environment：1973–1986. Environ. Toxic. Chem., 9：1245–2565.

Rouse, J. D. and Sabatini, D. A.（1993）：Minimizing surfactant losses using twin–head anionic surfactants in subsurface remediation. Environ. Sci. Technol., 27：2072–2078.

Rubio, J. A., GonzalezMazo, E. and GomezParra, A.（1996）：Sorption of linear alkalinebenzene sulfonates（LAS）on marine sediments. Marine Chem., 54：171–177.

Satake, I. and Yang, J. T.（1976）：Interaction of sodium decyl sulfate with poly（L–ornithine）and poly（L–lysine）in aqueous solution. Biopolymers, 15：2263–2275.

Sekiguchi, H., Miura, K., Oba, K. and Mori, A.（1975）：Biodegradation of α–Olefin sulfonates（AOS）and other surfactants. Yukagaku, 24：145–148.

Shirahama, K.（1974）：The binding equilibrium of sodium dodecyl sulfate to poly（ethylene oxide）in 0.1 M sodium chloride solution at 30°C. Colloid Polym. Sci., 252：978–981.

Shirahama, K.（1998）：The nature of polymer–surfactant interactions. *In* Polymer–surfactant systems, Surfactant

Science Series Vol. 77, Ed. Kwak, J. C.T., p.143–191. Marcel Dekker, New York.

Sullivan, W. T. and Swisher, R. D.（1969）：MBAS and LAS surfactants in Illinois river, 1968. Environmental Science Technol., 3：481–483.

Tabor, C. F. and Barber, L. B.（1996）：Fate of linear alkylbenzene sulfonate in the Mississipi River. Environ. Sci. Technol., 30：161–171.

Takada, H. and Ishiwatari, R.（1987）：Linear alkylbenzenes in urban riverine environments in Tokyo：Distribution, source and behavior. Environ. Sci. Technol., 21：875–883.

Tanaka, S., Oba, K., Fukushima, M., Nakayasu, K. and Hasebe, K.（1997）：Water solubility enhancement of pyrene in the presence of humic substances. Anal. Chim. Acta, 337：351–357.

West, C. C. and Harwell, J. H.（1992）：Surfactants and subsurface remediation. Environ. Sci. Technol., 26：2324–2330.

Westall, J. C., Chen, H., Zhang, W. and Brownawell, B. J.（1999）：Sorption of linear alkylbenzenesulfonates on sediment materials. Environ. Sci.Technol., 33：3110–3118.

Wolf, W. D. and Feijtel, T.（1998）：Terrestrial risk assessment for linear alkylbenzenesulfonate（LAS）in sludge–amended soils. Chemosphere, 36：1319–1343.

Yediler, A., Zhang, Y., Cai, J. and Korte, F.（1989）：Effect of the microbial population size on the degradation of linear alkylbenzene sulfonate in lake water（Dong Hu ＝ East Lake, Wuhan, Hubei, P.R. China）. Chemosphere, 18：1589–1597.

Yee, M. M., Miyajima, T. and Takisawa, N.（2009）：Study of ionic surfactants binding to humic acid and fulvic acid by potentiometric titration and dynamic light scattering. Colloids and Surfaces A, 347：128–132.

Zhao, B., Zhu, L. and Yang, K.（2006）：Solubilization of DNAPLs by mixed surfactant：Reduction in partitioning losses of non–ionic surfactant. Chemosphere, 62：772–779.

Zhu, L., Yang, K., Lou, B. and Yuan, B.（2003）：A multi–component statistic analysis for the influence of sediment/soil composition on the sorption of a nonionic surfactant（Triton X–100）onto sediments/soils. Water Res., 37：4792–4800.

要　　　旨

界面活性剤の吸着特性を明らかにするためには，土壌と水環境中での界面活性剤の挙動の理解が重要である．しかしながら，多腐植質土壌の吸着に関する研究は少ない．本研究では，アニオン性界面活性剤であるドデシルベンゼンスルホン酸の吸着を検討した．非アロフェン質黒ボク土を用いたのは，この土が多量の腐植質を含み，負荷電のみを有するためである．その結果，土粒子と界面活性剤の間には，電気的には反発力だけが生じる．吸着量は，土粒子表面近傍の電場を遮蔽し疎水的反応を強調するため，100 mmol L^{-1} NaCl の電解質濃度下で測定した．吸着等温線には Langmuir–Freundlich–Hill の式を用いて分析した．ドデシルベンゼンスルホン酸の吸着量は，低濃度領域において濃度の上昇とともに急激に増大した．この急激な増大は，吸着された界面活性剤の炭素鎖間の疎水性相互作用による協同吸着を示唆した．吸着量は土粒子と界面活性剤の間の静電的反発が減少するために，低 pH でより高い値となった．直鎖型炭素鎖を持つドデシルベンゼンスルホン酸の吸着は炭素鎖構造の違いにより，分岐型のそれよりも高い値を示した．

キーワード：アニオン性界面活性剤，静電的反発力，ドデシルベンゼンスルフォン酸ナトリウム，吸着等温線，黒ぼく土