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**Adsorption of Anionic Surfactant (Sodium Dodecyl Sulfate)  
on Silica**

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## ABSTRACT

The adsorption of an anionic surfactant sodium dodecyl sulfate (SDS) on a negatively charged silica was studied to provide a better understanding of surfactant adsorption phenomena in an electrostatic repulsion environment between surfactant and soil. The adsorption experiment was conducted under different electrolyte concentration and pH. Results indicated that adsorption happened with hydrophobic interaction although electrostatic repulsion generated between SDS and silica surface. The adsorption amount decreased with decreasing electrolyte concentration and increasing pH due to the increase of electrostatic repulsion. The influence of electric potential near the silica surface on the adsorption was confirmed with the modified Langmuir adsorption equation, 1-pK basic Stern model and the zeta potential. Because silica is ubiquitous in soils and water environment, the adsorption characteristics of an anionic surfactant is important when we consider the fate of an anionic surfactant in the environment. The result is also useful when considering the fate of agricultural chemicals which contain negative charge and hydrophobic sites.

**Key words:** 1-pK basic Stern model, adsorption, silica, sodium dodecyl sulfate, surface charge density, zeta potential

## 1. INTRODUCTION

Surfactants, the surface active agents, are amphiphilic compounds composed of hydrophilic head and hydrophobic tail. Its application has been a major topic of experimental and theoretical interest for many years in areas of enhanced oil recovery, soil remediation, formation of organic films, flotation, wetting, adhesion, detergency, and dispersion stability which are closely related to our life and environment (Wang and Kwak 1998). Conversely, because surfactant can destroy cells, it strongly affect living organisms and ecosystem (Sakashita, 1979).

A large number of studies on surfactants adsorption on solid-liquid interface had been reported (Hough DB and Rendall HM 1983; Koopal *et al.* 1995). Most studies focused on cationic surfactant adsorption on negatively charged solids (Goloub *et al.* 1996; Wangnerud and Olofsson 1992; Koopal *et al.* 2004; Ishiguro *et al.* 2007; Ishiguro and Koopal 2009, 2011), and adsorption of anionic surfactants was mostly studied on positive metal hydroxide surfaces (Mougdil *et al.* 1988; Bohmer and Koopal, 1992; Pham *et al.* 2015). Electrostatic repulsions between the surfactant and the surface occurs when anionic surfactants adsorb on anionic polymers; Ali *et al.* (1987) found that as the density of surface negative charge increased, the total adsorbed amount of anionic surfactants also increased within the range of surface charge densities between 0 and  $-0.85 \mu\text{C}/\text{cm}^2$ . This may be because of the electrostatic repulsions between the charged surface and the anionic head groups, causing the surfactant molecules to adsorb in a more extended conformation, thus allowing more molecules to contact the surface. However, Gwin (1988) found that for surface charge densities of  $-12.5$  and  $-13.5 \mu\text{C}/\text{cm}^2$ , the surfactant molecules were completely repelled by the electrostatic interactions with the surface. The results of Brouwer and Zsom (1987) indicated that electrostatic repulsion effects were significant for anionic surfactants adsorbing on polystyrene latex particles bearing anionic surface groups. In contrast with the results of Ali *et al.*, Brouwer and Zsom found that increased surface charge (in the range of  $-1.9$  to  $-15.0 \mu/\text{cm}^2$ ) resulted in a decrease in the adsorption amount.

Silica is a most commonly found mineral in soil and water environment and is negatively charged in natural condition. There are many studies about adsorption of cationic surfactants on silica, and

considerable adsorption amount was detected. However, because of the weak hydrophobic interaction and relatively strong electrostatic repulsion between silica surface and anionic surfactants, a few studies have focused on this theme. Nevskaja *et al.* (1998) showed that only small amount of anionic surfactants were adsorbed on a silica quartz and the amount increased with the increase of salt concentration. However, they only showed the surfactant adsorption at no NaCl addition and at 1 g NaCl/L; precise data for the influence of electrolyte was lacking and the pH influence was not observed. Moreover, there was no adsorption isotherm which could confirm a theoretical interpretation. Huang *et al.* (1989) and Somasundaran *et al.* (1990) found that the silica gel could adsorb an anionic surfactant when it was mixed with a cationic surfactant, although the anionic surfactant could not be easily adsorbed on the silica surface directly. In this case, the anionic surfactant was adsorbed on the hydrophobic part of the cationic surfactant which was directly adsorbed on the silica surface. The hydrophobic attraction and electrostatic interaction are important for an anionic surfactant adsorption on the negatively charged silica.

Sodium dodecyl sulfate (SDS) is an anionic surfactant with a simplest carbon chain structure. SDS is adsorbed on the surface of humic soil which is also negatively charged (Ishiguro *et al.* 2008). Because SDS is easily decomposed in the soil, its precise adsorption phenomenon cannot be indicated clearly. Previous studies for the adsorption of anionic surfactant on negatively charged silica surface only pointed out that it would barely happen in general. In this research, SDS adsorption on silica was systematically investigated under different pH and NaCl concentration which affected the electric potential near the silica surface. The influence of electric potential near the silica surface on the adsorption was elucidated by using theoretical adsorption equation, 1-pK basic Stern model, and zeta potential.

## 2. MATERIALS AND METHODS

### 2.1 Surfactant

An anionic surfactant, sodium dodecyl sulfate (SDS,  $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$ , molecular weight 288.38 g/mol) with purity of 99.0% was purchased from Nacalai Tesque, Inc. Kyoto, Japan. The critical micelle concentrations (CMC) of SDS at three sodium chloride concentrations at 25 °C obtained from the measurement with anionic surfactant-selective membrane method are shown in Table 1.

### 2.2 Silica

Porous silicon dioxide powder gels (Silica,  $\text{SiO}_2$ ) with a purity of 99.5% was purchased from Sigma-Aldrich Co. LLC. USA. The specific surface area was 414  $\text{m}^2/\text{g}$ , total pore volume was 0.87 ml/g obtained by BET method with BECKMAN COULTER SA 3100 Surface Area and Pore Size Analyzer. The mean diameter was 1.2  $\mu\text{m}$  measured by ultrasonic attenuation spectroscopy with Acoustic Electroacoustic Spectrometer (Dispersion Technology Model 1200).

### 2.3 Adsorption isotherms

Adsorption isotherms were obtained by a batch method at different conditions to investigate the influence of electrolyte concentration and pH on the SDS adsorption on silica. The silica was washed by 0.1 mol/L hydrochloric acid (HCl) for 3 times to remove impurity and saturate silica surface with  $\text{H}^+$ . The experiment was conducted under the conditions at 0.0001, 0.001, 0.01 and 0.1 mol/L NaCl at pH 4.5, and under the conditions at 0.1 mol/L NaCl at pH 3, 5, and 7 at  $25 \pm 1^\circ\text{C}$ . Five gram of the silica (dry weight basis) was placed in a 40 mL centrifuge tube and equilibrated with NaCl solutions with different

concentrations as mentioned above. Dilute HCl or sodium hydroxide (NaOH) solution were used to adjust the pH of silica colloidal suspension during the equilibration. The silica sample was centrifuged and the supernatant was discarded. Then, different concentrations of SDS solutions (concentrations ranging from 0.02 to 20.0 mmol/L) at the same NaCl concentrations as those of the former equilibrated solutions were added into the silica colloidal suspensions and were shaken for 5 min. After the mixture was well equilibrated, it was centrifuged for 10 min at 7000 rpm (HITACHI CR 20GIII). The supernatant was collected and the SDS concentration was measured with a homemade anionic surfactant-selective electrode (Fukui *et al.* 2003). The homemade concentration cell was constructed as follows: silver (Ag)/silver chloride (AgCl) electrode | agar bridge | reference solution ( $C_0$ ) | functional membrane | test solution ( $C_1$ ) | agar bridge | Ag/AgCl electrode, where  $C_0$  (1 mmol/L) and  $C_1$  are the concentrations of the surfactant in the reference solution and in the collected supernatant. The electromotive force (EMF) was measured by a digital voltmeter with high input impedance at  $25 \pm 1^\circ\text{C}$ . The EMF,  $E$ , can be expressed with the following equation:

$$E = S \log(C_1/C_0) \quad (1)$$

where  $S$  is the experimental slope. The theoretical value of  $S$  is 59.2 mV at  $25^\circ\text{C}$  (Nernstian slope). At each standard SDS concentration,  $E$  was measured and a relationship of EMF as a function of the logarithm of SDS concentration, a so-called calibration line, was obtained (Fukui *et al.* 2003; Ishiguro *et al.* 2007; Ishiguro and Koopal 2009; Ahmed *et al.* 2012b; Ahmed and Ishiguro 2015). Critical micelle concentration (CMC) was obtained at the bend in the calibration line (Ishiguro *et al.* 2007; Ishiguro and Koopal 2009). SDS adsorption was calculated by the following equation:

$$\text{adsorption}(\text{mmol} / \text{kg}) = \frac{\text{added}(\text{mmol}) - \text{conc.}(\text{mmol} / \text{L}) \times \text{volume}(\text{L})}{w(\text{kg})} \quad (2)$$

where, *added* is the amount of added surfactant, *conc.* is the measured surfactant concentration of the supernatant, *volume* is the solution volume and *w* is the measured dry soil weight.

#### 2.4 Zeta potential measurement

Zeta potential of the silica particles was measured at 0.001, 0.01 and 0.1 mol/L NaCl under different pH. The ratio of silica to solution in weight was set at about 1:20000 to get a good measurement result. It was obtained by measuring the electrophoretic mobility of the silica particles (Model 502, Nihon Rufuto). The zeta potential was calculated with Helmholtz-Smoluchowski equation, because the ratio of particle radius to the Debye length was larger than 100 (Hiemenz 1986) and the magnitude of zeta potential was smaller than 25 mV (Kobayashi 2014).

#### 2.5 Surface charge density measurement and modeling

The surface charge density of silica samples at different electrolyte concentrations were measured by acid base titration at  $25 \pm 1^\circ\text{C}$  with a pH meter. NaCl solutions as blank and equilibrated silica colloidal suspensions were used for the titration. The titrations were conducted at 0.01, 0.1 and 1 mol/L NaCl because the acid/base consumption by titration was not affected the electrolyte concentration. The solutions were prepared from  $\text{CO}_2$ -free boiled Milli-Q water. During the titrations, nitrogen gas ( $\text{N}_2$ ) was continuously flowed in the solutions to guarantee  $\text{CO}_2$ -free. Hydrochloric acid and sodium hydroxide solution of 0.01, 0.05 and 0.1 mol/L were used. The charge density,  $Z$ , was obtained by using the following equations.

$$C_{\text{coll}}Z = C'_a - C'_b - (C_a - C_b) \quad (3)$$

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where  $C_{coll}$  is the concentration of silica,  $C'$  is the acid/alkaline concentration after titration for the silica solution,  $C$  is the acid/alkaline concentration after titration for the blank solution, the subscript  $a$  is for acid and the subscript  $b$  is for alkaline (Kobayashi 2014).

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Experimental results were evaluated by 1-pK basic Stern model which has been used to rationalize the charging behavior of pH-dependent surface charge oxides (Hiemstra *et al.* 1989). When de-protonation of silanol groups ( $\equiv\text{Si-OH}$ ) happens on the surface of silica, we can draw the following processes:

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the amount of all the silanol groups per surface area,  $\Gamma_T$  ( $1/\text{m}^2$ ) is

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$$\Gamma_T = \Gamma_{\text{SiOH}} + \Gamma_{\text{SiO}^-} \quad (5)$$

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where  $\Gamma_{\text{SiOH}}$  is the amount of  $-\text{SiOH}$  per surface area and  $\Gamma_{\text{SiO}^-}$  is the amount of  $-\text{SiO}^-$  per surface area.

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The surface charge density,  $\sigma$  ( $\text{C}/\text{m}^2$ ), is

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$$\sigma = -e \Gamma_{\text{SiO}^-} \quad (6)$$

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where  $e$  is the elementary charge. According to mass action law for the reaction equilibrium, we obtain

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$$\frac{a_{\text{H}^+}^S \Gamma_{\text{SiO}^-}}{\Gamma_{\text{SiOH}}} = K = 10^{-pK} \quad (7)$$

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where  $K$  or  $10^{-pK}$  is the dissociation constant and  $a_{\text{H}^+}^S$  ( $\text{mol}/\text{L}$ ) is the activity of protons adjacent to the surface:

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$$a_{\text{H}^+}^S = a_{\text{H}^+} \exp\left(\frac{-e\Psi_0}{k_B T}\right) \quad (8)$$

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where  $a_{\text{H}^+}$  is the activity of proton in bulk solution,  $\Psi_0$  (V) is the surface potential,  $k_B$  is the Boltzmann constant and  $T$  is the absolute temperature. The surface charge density is written by the following equations.

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## 2.5 Calculation of potential distributions near the silica surface

To describe the potential distribution with distance in the diffuse layer from the outer surface of the Stern layer, Gouy-Chapman expression was introduced (Kobayashi *et al.* 2005; Kobayashi 2014):

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$$\Psi = \frac{4k_B T}{e} \arctan \left[ \tanh\left(\frac{ze\Psi_d}{4k_B T}\right) \exp(-\kappa x) \right] \quad (12)$$

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where  $\Psi$  is the potential at  $x$  from the outer surface of the Stern layer,  $z$  is the valence of the counter ion. By adding the vaules  $\Psi_d$  from 1-pK basic Stern model, the distribution of potentials with the distance was calculated.

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## 2.7 Adsorption isotherm

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The adsorption isotherms were evaluated with the Langmuir adsorption equation with potential modification (Ahmed and Ishiguro 2015):

$$q = Q \frac{KC}{1 + KC} \quad (13)$$

$$\Delta G \text{ (J/mol)} = RT \ln K \quad (14)$$

$$K = \alpha \exp\left(\frac{F\phi}{RT}\right) \quad (15)$$

where,  $q$  is the adsorption amount,  $Q$  is the maximum adsorption,  $C$  is the equilibrium SDS concentration (mol/L),  $K$  is the adsorption constant,  $\Delta G$  is the adsorption energy,  $\alpha$  is the intrinsic adsorption constant,  $\phi$  (V) is the adsorption site potential,  $F$  (C/mol) is the Faraday constant,  $R$  (J/(K·mol)) is the gas constant and  $T$  (K) is the absolute temperature. By using equation (13), the influence of the adsorption site potential was evaluated. The value  $\alpha$  was set as a constant value for all conditions. The  $Q$ ,  $\phi$  and  $\alpha$  were the parameters to obtain the best fitting adsorption isotherm with the measured values. The obtained value of  $Q$  was 0.7 mmol/kg and that of  $\alpha$  was  $4 \times 10^6$ .

### 3. RESULT

#### 3.1 SDS Adsorption Isotherms

Measured isotherms of SDS adsorption on silica at pH 4.5 and different electrolyte concentrations (NaCl) are shown in Fig. 1. Double log scale is presented in the coordinate. Adsorption experiment at NaCl concentration of 0.0001 mol/L and pH 4.5 was also conducted. However, the adsorption was not detected at this electrolyte concentration. The adsorption decreased with decreasing electrolyte concentration. Measured isotherms of SDS adsorption at 0.1 mol/L NaCl and different pH are shown in Fig. 2. The adsorption decreased with increasing pH.

Calculated SDS adsorption isotherms using the modified Langmuir equation are also shown in Figs. 1 and 2. The intrinsic adsorption constant,  $\alpha$ , was  $4 \times 10^6$  and the maximum adsorption,  $Q$ , was 0.7 mmol/kg for all conditions. The adsorption site potentials,  $\phi$ , are shown in Figs. 3 and 4. The calculated adsorption values agreed with the measured values as a whole (Figs 1 and 2). However, the trend was observed that the measured values at lower surfactant concentration showed steeper slope than unit. The magnitude of the calculated adsorption site potential increased with the decrease of the electrolyte concentration and the increase of the pH. It also increased with increasing SDS concentration.

#### 3.2 Surface charge density of silica

The measured surface charge density of silica as a function of pH at different NaCl concentrations are shown in Fig. 5. At smaller than pH 4, the silica was not negatively charged. The magnitude of the charge density increased with the increase of the pH and the increase of the electrolyte concentration, due to the existence of silanol groups ( $\equiv\text{Si-OH}$ ) and dehydration (Liu *et al.* 2009). These results are consistent with Kobayashi *et al.* (2005). At pH 4, the surface was saturated with hydroxyl groups. The pH here is the point of zero charge (pzc). The calculated charge density by using the 1-pK basic Stern model is also shown in Fig. 5. The physical parameters for the calculation were  $\text{pK}=4.7$ ,  $C_s=10 \text{ F/m}^2$ ,  $T_T=4.9/\text{nm}^2$  was used following the result of Zhuravlev (2000). The calculated values agreed with the measured values as a whole although the differences were observed at lower pH. The calculated potential distributions near the silica surface are shown in Figs. 6 and 7. The place at 0 nm is the outer surface of the Stern layer in the



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model. At pH 4.5, the magnitude of the potential of the outer surface of the Stern layer,  $\Psi_d$ , was larger as the electrolyte concentration decreased although the magnitude of surface charge density was larger as the electrolyte concentration increased. At 0.1 mol/L NaCl, the magnitude of the potential increased with the increase of pH.

### 3.3 Zeta potential of silica

The zeta potential distribution with the pH changes are compared among the different electrolyte concentrations as shown in Fig. 8. The isoelectric point was at around pH 2.2. At larger than this pH, the zeta potentials were all negative. With the increase of pH value, the magnitude of zeta potential increased, as expected from the surface charge density. The magnitude of the zeta potential was larger with decreasing the electrolyte concentration as a trend. Same result was shown by Kobayashi et al. (2005).

## 4. DISCUSSION

SDS adsorption increased with the decrease of pH (Fig. 2) and increase of electrolyte concentration (Fig. 1). SDS adsorbed with hydrophobic interaction because the silica had hydrophobic surface on siloxane groups,  $\equiv\text{Si-O-Si}\equiv$  (Hofmann *et al.* 1934; Laskorin *et al.* 1977). When the pH increases, protons in silanol groups,  $\equiv\text{Si-OH}$ , are released from the surface and the negative charge increases as the measured charge density shows (Fig. 5, Eqs. 4).

As shown in the theoretical adsorption Eqs. (13) and (15), the SDS adsorption,  $q$ , is determined only with the adsorption site potential,  $\phi$ , at certain pH, electrolyte concentration and SDS concentration,  $C$ ; only  $\phi$  is the parameter because the maximum adsorption,  $Q=0.7$  mmol/kg, and the intrinsic adsorption parameter,  $\alpha=4\times 10^6$  are the constant values under different solution conditions. The proper agreement between measured and calculated SDS adsorptions in Figs. 1 and 2 justifies the application of the theoretical adsorption equation. From the adsorption equation, we can understand that the SDS adsorption becomes larger when  $\phi$  becomes larger, because SDS is negatively charged. Because the magnitude of the negative potential near the silica surface increases with the increase of pH, the electrostatic repulsive force between SDS and the silica increases and the adsorption decreases. The increase of the negative potential with the increase of pH is confirmed with the measured zeta potential (Fig. 8), the calculated adsorption site potential with the Langmuir equation (Fig. 4) and the calculated potential near the surface with 1-pK basic Stern model (Fig. 7). When the electrolyte concentration increases, the magnitude of the negative potential near the surface decreases due to the screening effect. Then, the repulsive force between SDS and the silica surface decreases and SDS adsorption increases. The decrease of the magnitude of the negative potential is also confirmed with the calculated adsorption site potential with the Langmuir equation (Fig. 3) and the calculated potential near the surface with 1-pK basic Stern model (Fig. 6). The measured zeta potential (Fig. 8) also shows this trend. Although the magnitude of negative charge density increases with the increase of the electrolyte concentration (Fig. 5), the electrostatic repulsion becomes smaller with the increase of the electrolyte concentration, because the screening effect is strong and the magnitude of the potential near the surface decreases as shown in Fig. 6. When the pH increases and/or the electrolyte concentration decreases, SDS adsorption decreases, and finally the adsorption cannot be detected, because adsorption site potential decreases and electrostatic repulsion becomes stronger than the hydrophobic attraction.

Because the length of the hydrophobic tail of SDS is about 1.5 nm when it stretches, the charged head of SDS locates within the length. The calculated potentials within that range of DDL are almost same

with the calculated adsorption site potentials with the Langmuir equation at pH 5 and pH 7. The zeta potentials are smaller than them but the differences are not large. However the calculated potentials in the range of DDL are much smaller at pH 3 and pH 4.5 because 1-pK basic Stern model results are not agreed well at lower pH as shown in Fig. 5. The magnitude of adsorption site potential increased with the increase of SDS concentration because SDS adsorption increased with the increase of SDS concentration.

The adsorption energy of SDS on the silica surface without electric potential can be calculated with equation (14) and the intrinsic adsorption constant,  $\alpha$ . As  $\alpha$  is  $4 \times 10^6$ , the adsorption energy,  $\Delta G = RT \ln \alpha$ , becomes  $15.2RT$  J/mol =  $15.2k_B T$  J/molecule, where  $k_B$  is Boltzmann constant. Because SDS has 12 carbon chains, the intrinsic adsorption energy per  $\text{CH}_2$  is  $15.2/12 = 1.27k_B T$  J. The value is closer to the value,  $0.97 k_B T$  J, obtained by other researchers (Somasundaran et al. 1964). This similarity confirms the result of the adsorption isotherm.

The slope of the SDS isotherm at lower SDS concentration showed larger than unit (Fig. 1 and Fig. 2). This indicates the cooperative adsorption which is generated by the lateral attraction among the hydrophobic tails of SDS. The decrease of anionic surfactant adsorption with the increase of pH and/or the decrease of the electrolyte concentration and the cooperative adsorption at lower surfactant concentration was also observed for highly humic soil by Ahmed *et al.* (2012a) and Ahmed and Ishiguro (2015). However, the adsorption amount was much larger because the highly humic soil has much amount of hydrophobic surface. Nevskaja *et al.* (1998) showed the similar result of the increase of anionic surfactant adsorption with the increase of electrolyte concentration for silica quartz. Somasundaran *et al.* (1990) pointed out that no significant adsorption of anionic surfactant, sodium dodecyl benzenesulfonate (SDBS) on silica with a surface area of  $25 \text{ m}^2/\text{g}$  could be detected, however the mixture of a non-ionic surfactant, octaethylene glycol mono-*n*-dodecyl ether and SDBS showed a strong adsorption onto silica. Huang *et al.* (1989) also came out this result by using SDS and silica gel. They mixed the SDS with a cationic surfactant, dodecyl trimethylammonium bromide (DTAB). No significant adsorption of anionic surfactants can be detected, but in the mixed systems, the adsorption amount of both cationic and anionic surfactant ions are enhanced. The surface areas of silica in studies are much smaller than that in our study. This is supposed to cause the different result. Nicholas *et al.* (1996) indicated the pH effect on the adsorption of an anionic surfactant (4-<sub>11</sub>-paraxylene sulfonate) on alumina ( $\text{Al}_2\text{O}_3$ ) with a point of zero charge of pH 8.5. At low pH, the adsorption was relatively considerable as the alumina was positively charged, as the pH increases, the adsorption started to decrease before pH 8.5 (the pzc), passed through an observable kink at pH 9.7, and then decreased fairly rapidly. The adsorption was observed in the negatively charged region of the alumina although the adsorption amount was small. Same results had also been found by Denoyel and Rouquerol (1991). Their conclusions also indicated the importance of hydrophobic force.

In this study, the physical parameters for the surface charge density modeling were  $\text{pK}=4.7$ ,  $C_S = 10 \text{ F/m}^2$ ,  $\Gamma_T = 4.9/\text{nm}^2$ . Which are quite different from that of Hiemstra *et al.* (1989) and Kobayashi *et al.* (2005), with a  $\text{pK}=7.5$ ,  $C_S = 2.9 \text{ F/m}^2$ ,  $\Gamma_T = 8/\text{nm}^2$ . The difference is supposed to come from the difference of pore structure of the silica. The silica used here has the pore volume of  $0.87 \text{ ml/g}$ , which is larger than the other silica productions used. In this study  $\Gamma_T = 4.9/\text{nm}^2$  was used following the result of Zhuravlev (2000).

## 5. CONCLUSION

In spite of electrostatic repulsion between negatively charged SDS and silica surface, adsorption

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3 277 happens. Silica adsorbs SDS because it has hydrophobic surface on silixane. When pH increases and/or  
4 278 electrolyte concentration decreases, SDS adsorption on the silica decreases due to the increase of  
5 279 electrostatic repulsion. When the repulsion becomes larger, SDS adsorption cannot be detected. The  
6 280 influence of pH and electrolyte concentration through electric potential on SDS adsorption was confirmed  
7 281 with the measured zeta potential, the modified Langmuir equation and 1-pK basic Stern model. Silica is  
8 282 ubiquitous in soils and it adsorbs surfactants even it has a negative charge under the condition that the  
9 283 electrostatic repulsion is weak. It must be taken into account when we consider the fate of anionic  
10 284 surfactants in soils. The result is also useful when considering the fate of agricultural chemicals which  
11 285 contain negative charge and hydrophobic sites.

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3 **Table 1.** Critical Micelle Concentrations of SDS  
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NaCl, mol/L	CMC, mmol/L
0.1	1.3
0.01	3.3
0.001	5.4

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1 **Figure 1.** Isotherms of SDS adsorption on silica at pH 4.5 and different electrolyte concentrations.  
2 The experimental result of NaCl solution is indicated with 0.001mol/L ( $\square$ ), 0.01 mol/L ( $\Delta$ ) and 0.1mol/L ( $\circ$ ). Lines  
3 present calculated ones with Langmuir equation with 0.001mol/L (—), 0.01 mol/L (---) and 0.1mol/L (-·-·-).

4  
5 **Figure 2.** Isotherms of SDS adsorption on silica at different pH values and the same NaCl concentration of 0.1 mol/L.  
6 The measured values are indicated with pH3 ( $\square$ ), pH5 ( $\circ$ ) and pH7 ( $\Delta$ ). The calculated values with Langmuir  
7 equation are indicated with pH3 (—), pH5 (-·-·-) and pH7 (---).

8  
9 **Figure 3.** Calculated site potential as a function of SDS equilibrium concentration at pH 4.5 and different NaCl  
10 concentrations.  
11 Lines present 0.001mol/L (—), 0.01 mol/L (---) and 0.1mol/L (-·-·-).

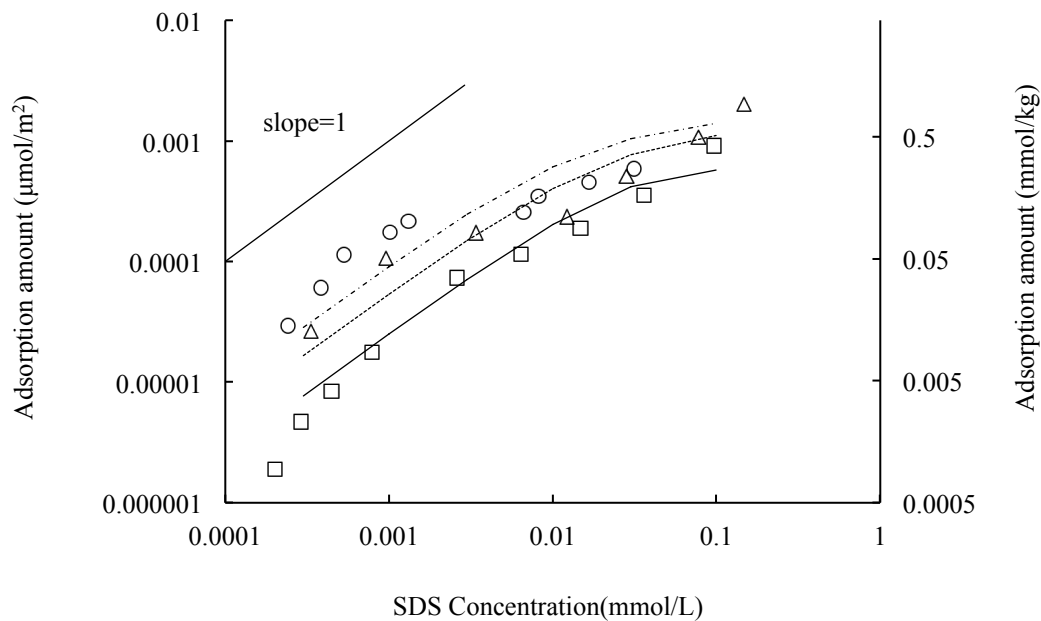
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13 **Figure 4.** Calculated site potential as a function of SDS equilibrium concentration at different pH values and the same  
14 NaCl concentration of 0.1 mol/L.  
15 Lines present pH3 (—), pH5 (-·-·-) and pH7 (---).

16  
17 **Figure 5.** Surface charge density of silica. Symbols are measured values and the solid lines are calculated values by  
18 1-pK basic Stern model.

19  
20 **Figure 6.** Calculated potential distributions near the silica surface without SDS at pH 4.5 and different NaCl  
21 concentrations.  
22 Lines present 0.01 mol/L (---), 0.1mol/L (-·-·-) and 1mol/L (—).

23  
24 **Figure 7.** Calculated potential distributions near the silica surface without SDS at different pH values and the same  
25 NaCl concentration of 0.1 mol/L.  
26 Lines present pH3 (—), pH4.5 (---), pH5 (-·-·-) and pH7 (- - -).

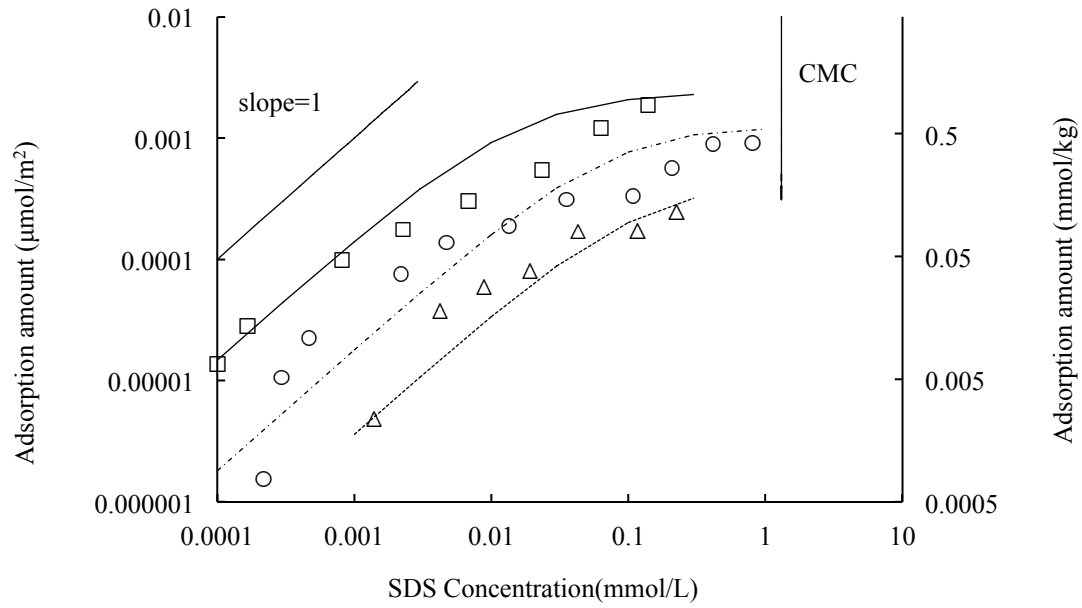
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28 **Figure 8.** Zeta potential as a function of pH under different electrolyte concentrations.



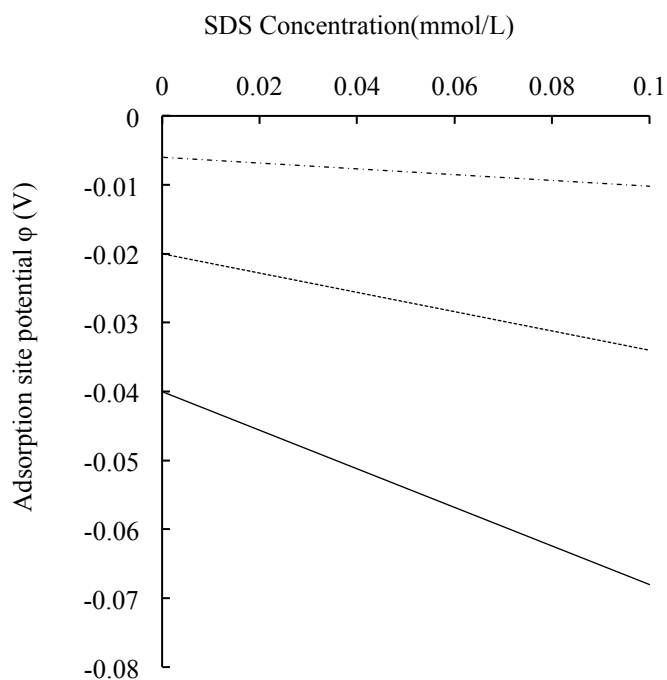
**Figure 1.** Isotherms of SDS adsorption on silica at pH 4.5 and different electrolyte concentrations. The experimental result of NaCl solution is indicated with 0.001mol/L ( $\square$ ), 0.01 mol/L ( $\triangle$ ) and 0.1mol/L ( $\circ$ ). Lines present calculated ones with Langmuir equation with 0.001mol/L (—), 0.01 mol/L (---) and 0.1mol/L (-·-·-).

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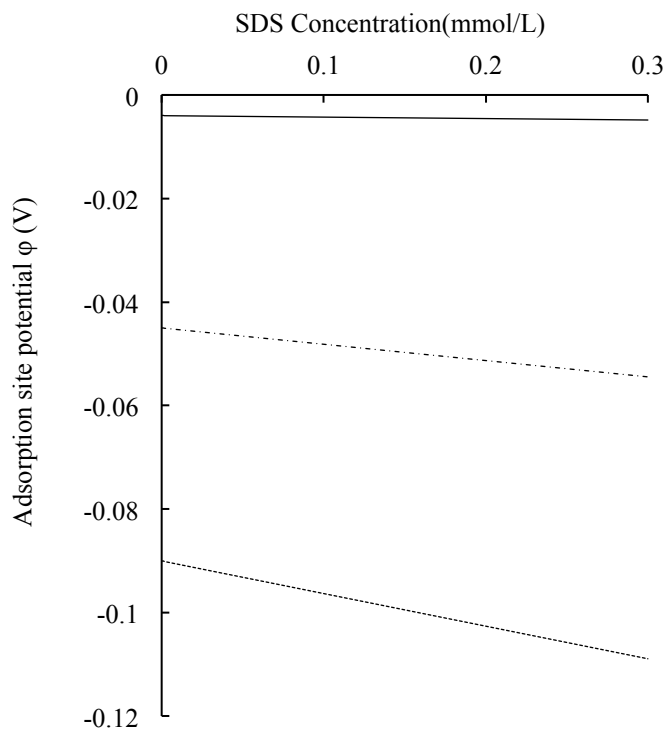


**Figure 2.** Isotherms of SDS adsorption on silica at different pH values and the same NaCl concentration of 0.1 mol/L. The measured values are indicated with pH3 ( $\square$ ), pH5 ( $\circ$ ) and pH7 ( $\Delta$ ). The calculated values with Langmuir equation are indicated with pH3 (—), pH5 (---) and pH7 (....).

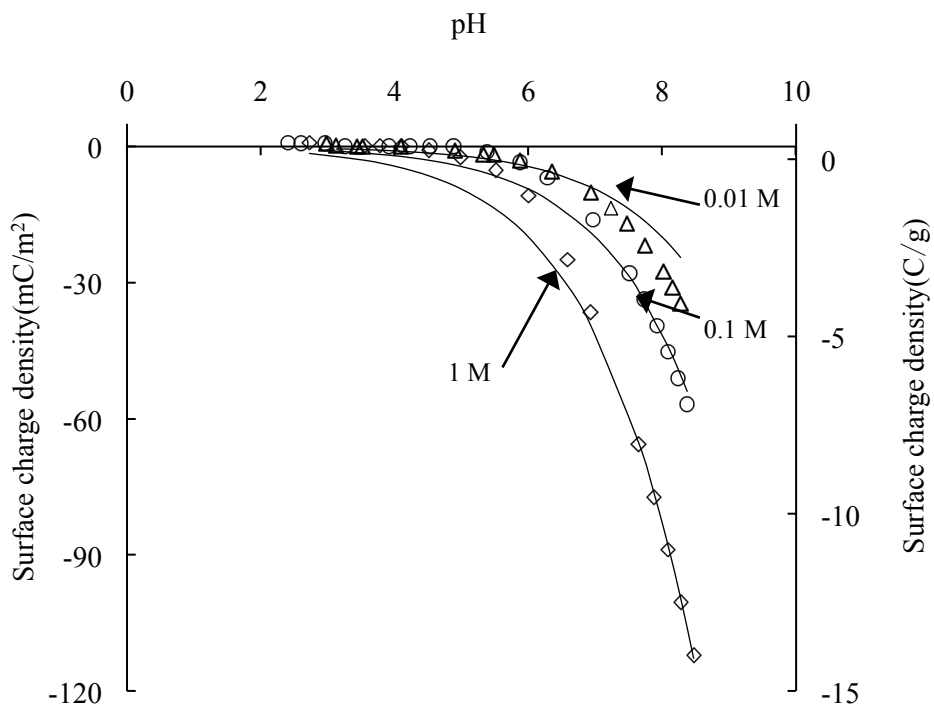


**Figure 3.** Calculated site potential as a function of SDS equilibrium concentration at pH 4.5 and different NaCl concentrations.

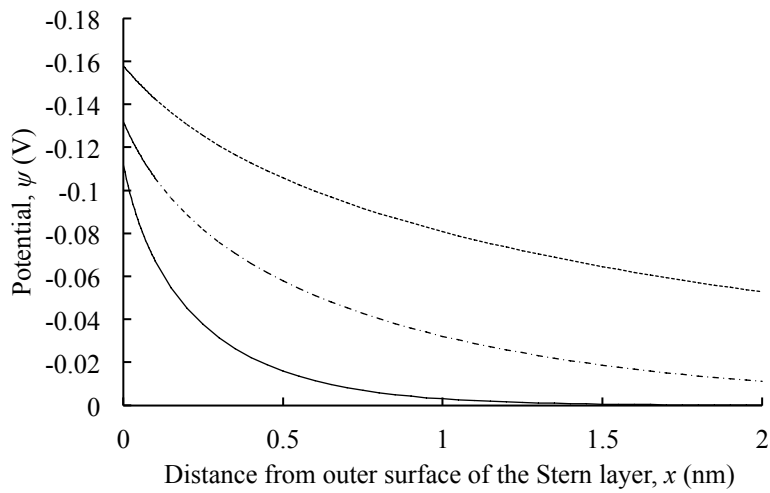
Lines present 0.001 mol/L (—), 0.01 mol/L (---) and 0.1 mol/L (-·-·-).



**Figure 4.** Calculated site potential as a function of SDS equilibrium concentration at different pH values and the same NaCl concentration of 0.1 mol/L. Lines present pH3 (—), pH5 (---) and pH7 (····).

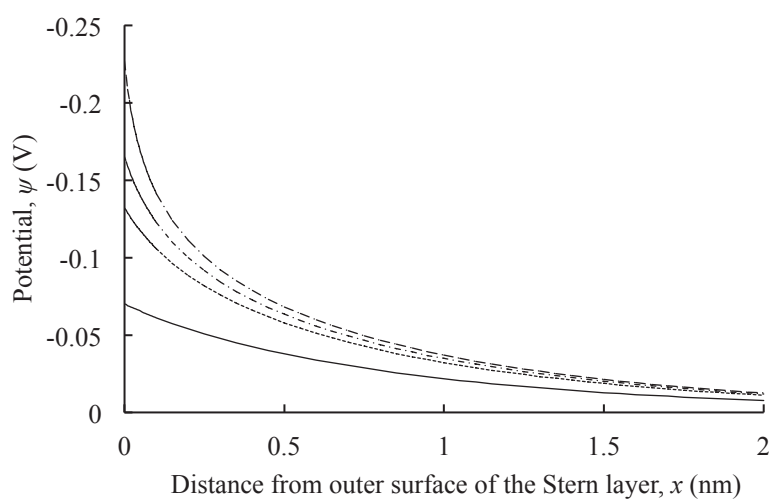


**Figure 5.** Surface charge density of silica. Symbols are measured values and the solid lines are calculated values by 1-pK basic Stern model.



**Figure 6.** Calculated potential distributions near the silica surface without SDS at pH 4.5 and different NaCl concentrations.

Lines present 0.01 mol/L (----), 0.1mol/L (-·-·-) and 1mol/L (—).



**Figure 7.** Calculated potential distributions near the silica surface without SDS at different pH values and the same NaCl concentration of 0.1 mol/L.

Lines present pH3 (—), pH4.5 (---), pH5 (-·-·-) and pH7 (- - -).

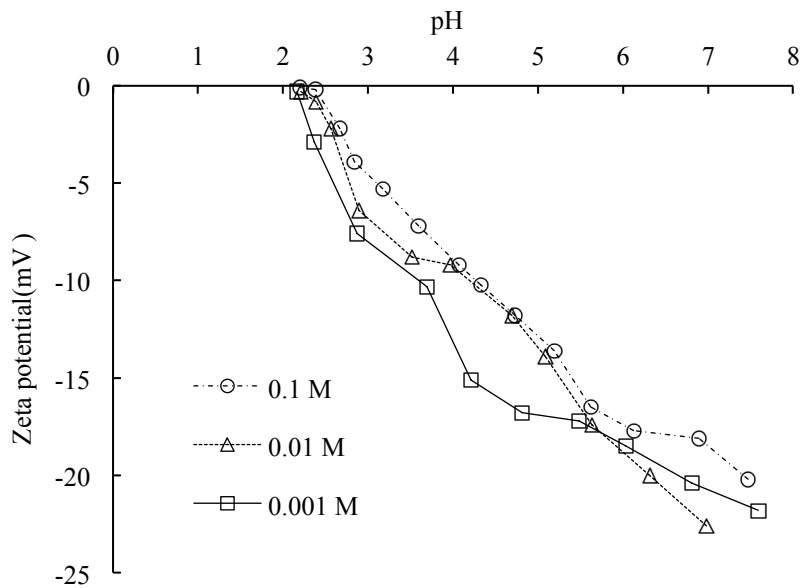


Figure 8. Zeta potential as a function of pH under different electrolyte concentrations.