



Title	Adsorption of anionic surfactant (sodium dodecyl sulfate) on silica
Author(s)	Li, Pengxiang; Ishiguro, Munehide
Citation	Soil science and plant nutrition, 62(3), 223-229 https://doi.org/10.1080/00380768.2016.1191969
Issue Date	2016-06
Doc URL	http://hdl.handle.net/2115/66427
Rights	This is an Accepted Manuscript of an article published by Taylor & Francis in Soil science and plant nutrition on 04 Jul 2016, available online: http://www.tandfonline.com/10.1080/00380768.2016.1191969 .
Type	article (author version)
File Information	Soil Sci. Plant Nutr.62-3_223-229.pdf



[Instructions for use](#)



Adsorption of Anionic Surfactant (Sodium Dodecyl Sulfate) on Silica

Journal:	<i>Soil Science and Plant Nutrition</i>
Manuscript ID	SSPN-16-038-F.R5
Manuscript Type:	Full-length paper
Date Submitted by the Author:	16-May-2016
Complete List of Authors:	Li, Pengxiang; Hokkaido University, Graduate School of Agriculture Ishiguro, Munehide; Hokkaido University, Research faculty of Agriculture
Keywords:	physical phenomena < Soil Physics, environmental conservation < Environment

SCHOLARONE™
Manuscripts

1
2
3 **0. Type of the paper:** Original article

4 **1. Title of the paper:** Adsorption of Anionic Surfactant (Sodium Dodecyl Sulfate) on Silica

5 **Running title:** Adsorption of sodium dodecyl sulfate on silica

6
7 **2. Names of the authors:**

8 Pengxiang Li^{1,*} (Corresponding author)

9 Munehide Ishiguro¹

10
11 **3. Addresses of the institutions:**

12 ¹Laboratory of Soil Conservation, Graduate School of Agriculture, Hokkaido University

13 Kita 9 Nishi 9, Kita-ku, Sapporo 060-8589, Japan

14
15 **4. Contact information of corresponding author:**

16 Name: Pengxiang Li

17 Postal address: ¹Laboratory of Soil Conservation, Graduate School of Agriculture, Hokkaido University

18 Kita 9 Nishi 9, Kita-ku, Sapporo 060-8589, Japan

19 E-mail: elephant@env.agr.hokudai.ac.jp

20 Fax: +81-11-706-2494

21 Tel: +81-080-1107-4317
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

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 $-15.0 \mu\text{C}/\text{cm}^2$) 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, SiO_2) with a purity of 99.5% was purchased from Sigma-Aldrich Co. LLC. USA. The specific surface area was 414 m^2/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 μm 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 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°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 CO_2 -free boiled Milli-Q water. During the titrations, nitrogen gas (N_2) was continuously flowed in the solutions to guarantee 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.

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

1
2
3
4
5
6

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

7
8
9
10

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

11



12

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

13

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

14

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

15

131 The surface charge density, σ (C/m^2), is

16

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

17

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

18

19

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

20

21

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

22

23

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

24

25

138 where a_{H^+} is the activity of proton in bulk solution, Ψ_0 (V) is the surface potential, k_B is the Boltzmann
139 constant and T is the absolute temperature. The surface charge density is written by the following
140 equations.

26

27

28

29

$$\sigma = C_S (\Psi_0 - \Psi_d) \quad (9)$$

30

31

$$\sigma = -\sigma_d = \left(\frac{2\varepsilon\kappa k_B T}{e}\right) \sinh\left(\frac{e\Psi_d}{2k_B T}\right) \quad (10)$$

32

33

34

141 where C_S (F/m^2) is the Stern layer capacitance, Ψ_d is the potential at the outer surface of Stern layer (the
142 diffuse layer potential), ε (F/m) is the permittivity of solvent (water), κ ($1/\text{m}$) is the Debye-Hückel
143 parameter and σ_d (C/m^2) is the charge density in the diffuse layer. The details of the model is written in
144 Kobayashi *et al.* (2005) and Kobayashi (2014, 2016).

35

36

37

38

148 2.5 Calculation of potential distributions near the silica surface

39

40

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

41

42

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

43

44

151 where Ψ is the potential at x from the outer surface of the Stern layer, z is the valence of the counter ion.
152 By adding the vaules Ψ_d from 1-pK basic Stern model, the distribution of potentials with the distance was
153 calculated.
154

45

46

47

48

155 2.7 Adsorption isotherm

49

50

51

52

53

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, ΔG is the adsorption energy, α is the intrinsic adsorption constant, ϕ (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 α was set as a constant value for all conditions. The Q , ϕ and α 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 α was 4×10^6 .

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, α , was 4×10^6 and the maximum adsorption, Q , was 0.7 mmol/kg for all conditions. The adsorption site potentials, ϕ , 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

1
2
3 194
4 195
5 196
6 197

model. At pH 4.5, the magnitude of the potential of the outer surface of the Stern layer, Ψ_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.

8
9 198

3.3 Zeta potential of silica

10 199
11 200
12 201
13 202
14 203

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).

17 204

4. DISCUSSION

18 205
19 206
20 207
21 208
22 209

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).

23 210
24 211
25 212
26 213
27 214
28 215
29 216
30 217
31 218
32 219
33 220
34 221
35 222
36 223
37 224
38 225
39 226
40 227
41 228
42 229
43 230
44 231
45 232

As shown in the theoretical adsorption Eqs. (13) and (15), the SDS adsorption, q , is determined only with the adsorption site potential, ϕ , at certain pH, electrolyte concentration and SDS concentration, C ; only ϕ 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 ϕ 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.

46 233
47 234

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, α . As α is 4×10^6 , 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 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-*11*-paraxylene sulfonate) on alumina (Al_2O_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 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

1
2
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.

15 286 ACKNOWLEDGMENT

16 287 This research was supported by Grants-in-Aid for Scientific Research (No. 25252042) from the Japan
17 288 Society for the Promotion of Science. Fund from Hokkaido University and China Scholarship Council
18 289 (CSC). Many thanks are extended to Professor Luuk K. Koopal in Wageningen University and Professor
19 290 Keishiro Shirahama in Saga University, for their valuable discussion on experimental parts. Also Mr
20 291 Zigong Ning and Shigeyori Kosugi for their help during the experiments.

24 292 REFERENCES

- 25 293 Ahmed F, Ishiguro M 2015: Effect of adsorption site potential on adsorption of sodium
26 294 dodecylbenzenesulfonate in highly humic volcanic ash soil. *Soil Science and Plant Nutrition.*, **61**,
27 295 432-439.
- 28 296 Ahmed F, Ishiguro M, Akae T 2012a: Dissolution of humic substances from highly humic volcanic ash
29 297 soil as affected by anionic surfactant, electrolyte concentration and pH. *J. Environ. Protect.*, **3**,
30 298 280-287.
- 31 299 Ahmed F, Ishiguro M, Moriguchi K, Akae T 2012b: Adsorption of sodium dodecylbenzene sulfonate on
32 300 highly humic non-allophanic andisol at high-electrolyte concentration. *J. Japanese Soc. Soil Phys.*, **123**,
33 301 45-54.
- 34 302 Ali SI, Steach JC, Zollars RL 1987: Effects of ionizable groups on the adsorption of surfactants onto latex
35 303 particle surfaces. *Colloids and Surfaces.*, **26**, 1-18
- 36 304 Böhmer MR, Koopal LK 1992: Adsorption of ionic surfactants on variable-charge surfaces. 1. charge
37 305 effects and structure of the adsorbed layer. *Langmuir.*, **8**, 2649-2659.
- 38 306 Brouwer WM, Zsom, RLJ 1987: Polystyrene Latex Particle Surface Characteristics. *Colloids and Surfaces.*,
39 307 **24**, 195.
- 40 308 Denoyel R, Rouquerol J 1991: Thermodynamic (including microcalorimetry) study of the adsorption of
41 309 nonionic and anionic surfactants onto silica, kaolin, and alumina. *Journal of Colloid and Interface*
42 310 *Science.*, 143, 555-572.
- 43 311 Fukui H, Kaminaga A, Maeda T, Hayakawa T 2003: Preparation of surfactant anion-selective electrodes
44 312 with different selectivity coefficients and a trial to determine each component in binary surfactant
45 313 mixtures. *Analytica Chimica Acta.*, **481**, 221-228.
- 46 314 Goloub TP, Koopal LK, Bijsterbosch BH, Sidorova MP 1996: Adsorption of cationic surfactants on silica.
47 315 surface charge effects. *Langmuir.*, **12**, 3188-3194.
- 48 316 Gwin JL 1988: Effect of Ionizable Surface Groups on the Adsorption of Linear Alkyl Sulfates on
49 317 Polystyrene Latex Surfaces, *M.S. thesis, Washington State University.*

- 1
2
3 318 Hiemenz PC 1986: Principles of colloid and surface chemistry. Chap 13. *Marcel Dekker/ New York*
- 4 319 Hiemstra T, Van Riemsdijk WH, Bolt GH 1989: Multisite proton adsorption modeling at the solid/solution
5 320 interface of (hydr)oxides: A new approach: I. Model description and evaluation of intrinsic reaction
6 321 constants. *Journal of Colloid and Interface Science.*, **133**, 91-104.
- 7 322 Hofmann U, Endell K, Wilm D 1934: X-ray and colloid-chemical investigations on clays. *Angew.Chem.*,
8 323 **47**, 539-547.
- 9 324 Hough DB, Rendall HM 1983: Adsorption from solution at the solid/liquid interface. Chap 6. *Academic*
10 325 *Press, London/New York.*
- 11 326 Huang Z, Yan ZL, Gu TR 1989: Mixed adsorption of cationic and anionic surfactants from aqueous
12 327 solution on silica gel. *Colloids and Surfaces.*, **36**, 353-358.
- 13 328 Ishiguro M, Koopal LK 2011: Predictive model of cationic surfactant binding to humic substances.
14 329 *Colloids and Surfaces A.*, **379**, 70-78.
- 15 330 Ishiguro M, Koopal LK 2009: Binding of alkylpyridinium chloride surfactants to sodium polystyrene
16 331 sulfonate. *Colloids and Surfaces A.*, **347**, 69-75.
- 17 332 Ishiguro M, Tan WF, Koopal LK 2007: Binding of cationic surfactants to humic substances. *Colloids and*
18 333 *Surfaces A.*, **306**, 29-39.
- 19 334 Ishiguro M, Torigoe T, Kameoka Y, Akae T 2008: Linear Anionic Surfactant (SDS) Transport in High
20 335 Humic Volcanic Ash Soil and its Permeability. *Irrigation, Drainage and Rural Engineering J.*, **76**,
21 336 485-491. (in Japanese with English summary)
- 22 337 Kobayashi M 2014: Soil and related interfacial electric phenomena. 4. Measurement and modeling of
23 338 surface charge. *J. Soil Sci. Plant Nutr.*, **85**, 258-263. (in Japanese)
- 24 339 Kobayashi M, Skarba M, Galletto P, Cakara D, Borkovec M 2005: Effects of heat treatment on the
25 340 aggregation and charging of Stöber-type silica. *Journal of Colloid and Interface Science.*, **292**,
26 341 139-147.
- 27 342 Koopal LK, Lee EM, Böhmer MR 1995: Adsorption of cationic and anionic surfactants on charged
28 343 metal-oxide surfaces. *J. Colloid Interface Sci.*, **170**, 85-97.
- 29 344 Koopal LK, Goloub TP, Davis TA 2004: Binding of ionic surfactants to purified humic acid. *J Colloid*
30 345 *Interface Sci.*, **275**, 360-7.
- 31 346 Laskorin BN, Strelko VV, Strazhesko DN, Denisov VI 1977: Sorbents on Basis of Silica Gels in
32 347 Radiochemistry, Atomizdat. in: *B.N. Laskorin (Ed.), Moscow.*
- 33 348 Liu P, Wang QS, Li X, Zhang CC 2009: Investigation of the states of water and OH groups on the surface
34 349 of silica. *Colloids and Surfaces A.*, **334**, 112-115.
- 35 350 Moudgil BM, Heriban S, Somasundaran P 1988: Adsorption of surfactants on minerals. Reagents in
36 351 Mineral Technology, Surfactant Science Series, *27Marcell Dekker, New York*, 79-101.
- 37 352 Nevskaiia DM, Guerrero-Ruiz A, Lopez-Gonzalez JD 1998: Adsorption of polyoxyethylenic nonionic and
38 353 anionic surfactants from aqueous solution: Effects induced by the addition of NaCl and CaCl₂. *Journal*
39 354 *of Colloid and Interface Science.*, **205(1)**, 97-105.
- 40 355 Nicholas PH, John HO'H, Jeffrey HH 1996: Modeling effects of ph and counterions on surfactant
41 356 adsorption at the oxide/water interface. *Ind. Eng. Chem. Res.*, **35**, 2844-2855.
- 42 357 Pham TD, Kobayashi M, Adachi Y 2015: Adsorption of anionic surfactant sodium dodecyl sulfate onto
43 358 alpha alumina with small surface area. *Colloid Polym. Sci.*, **293**, 217-227.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

359 Sakashita S 1979: Electron microscopic study of liver tissue after cutaneous administration of detergents. *J.*
360 *Clin. Electron Microscopy.*, **12**, 189-216.

361 Somasundaran P, Snell ED, Fu E, Xu Q 1990: Effect of adsorption of non-ionic surfactant and
362 non-ionic-anionic surfactant mixtures on silica-liquid interfacial properties. *Colloids and Surfaces.*, **63**,
363 49-54.

364 Somasundaran P,, Healy TW, Fuerstenau DW 1964: Surfactant Adsorption at the Solid—Liquid
365 Interface—Dependence of Mechanism on Chain Length. *J. Phys. Chem.*, **68**, 3562–3566

366 Wang W, Kwak JCT 1998: Adsorption at the alumina–water interface from mixed surfactant solutions.
367 *Colloids and Surfaces A: Physicochemical and Engineering Aspects.*, **156**, 95-110.

368 Wängnerud P, Olofsson G 1992: Adsorption isotherms for cationic surfactants on silica determined by *in*
369 *situ* ellipsometry. *Journal of Colloid and Interface Science.*, **153**, 392-398.

370 Zhuravlev LT 2000: The surface chemistry of amorphous silica. Zhuravlev model. *Colloids and Surfaces*
371 *A.*,**173**, 1-38

1
2
3 **Table 1.** Critical Micelle Concentrations of SDS
4

NaCl, mol/L	CMC, mmol/L
0.1	1.3
0.01	3.3
0.001	5.4

5
6
7
8
9
10
11 2
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

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 (Δ) 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 (Δ). 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 (-·-·-).

12
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 (- - -).

27
28 **Figure 8.** Zeta potential as a function of pH under different electrolyte concentrations.

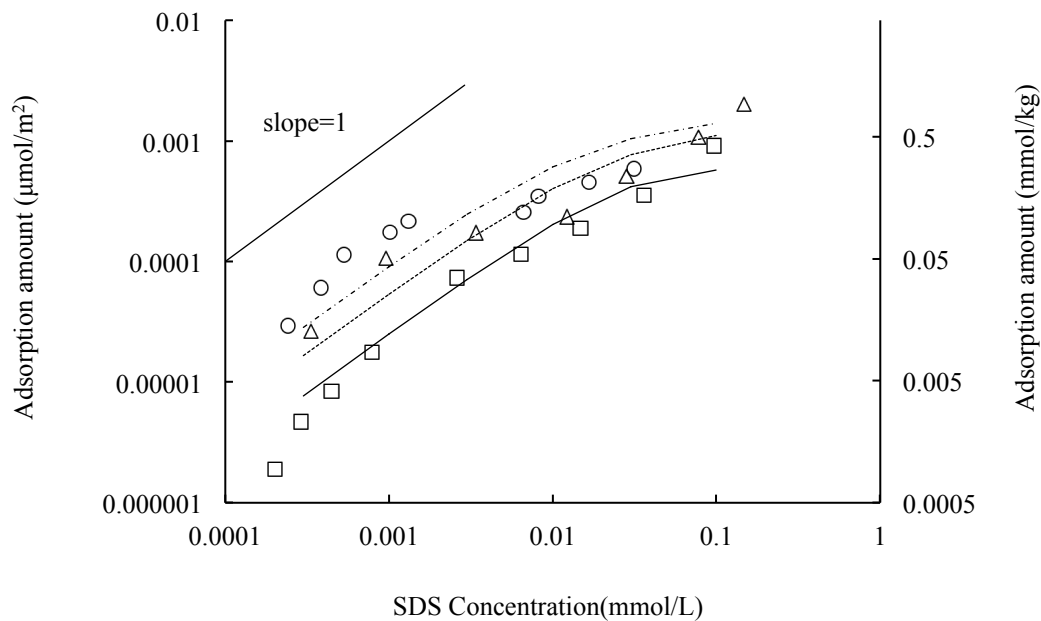


Figure 1. Isotherms of SDS adsorption on silica at pH 4.5 and different electrolyte concentrations. The experimental result of NaCl solution is indicated with 0.001mol/L (\square), 0.01 mol/L (Δ) and 0.1mol/L (\circ). Lines present calculated ones with Langmuir equation with 0.001mol/L (—), 0.01 mol/L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

29
30
31
32
33

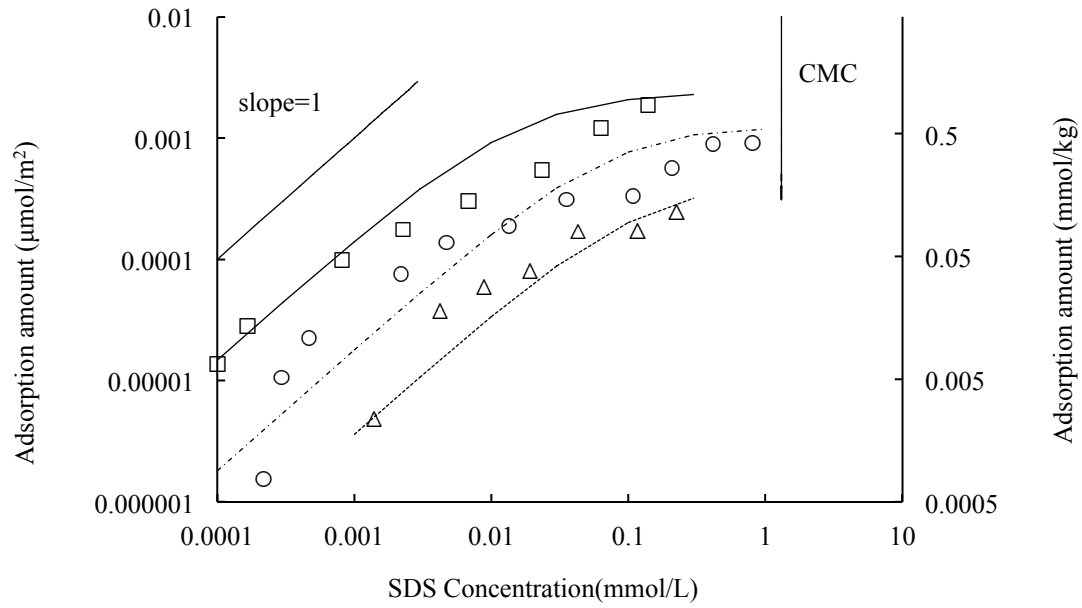


Figure 2. Isotherms of SDS adsorption on silica at different pH values and the same NaCl concentration of 0.1 mol/L. The measured values are indicated with pH3 (\square), pH5 (\circ) and pH7 (Δ). The calculated values with Langmuir equation are indicated with pH3 (—), pH5 (---) and pH7 (....).

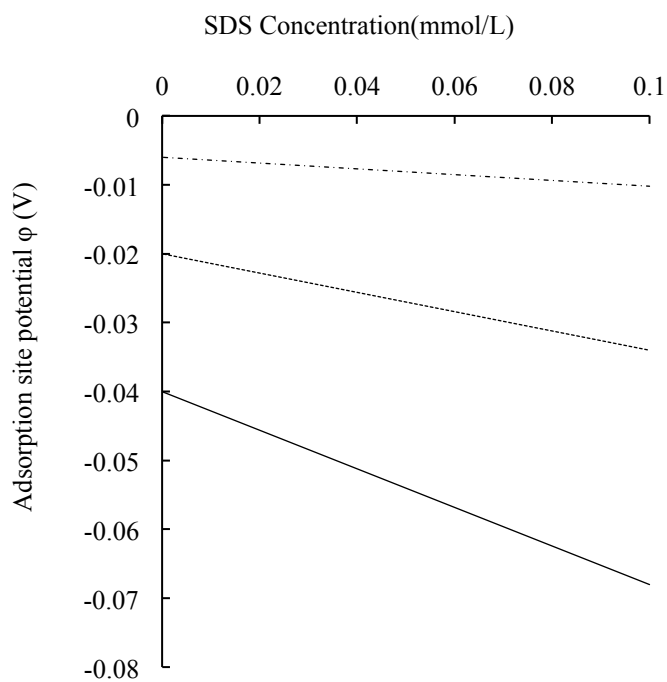


Figure 3. Calculated site potential as a function of SDS equilibrium concentration at pH 4.5 and different NaCl concentrations.

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

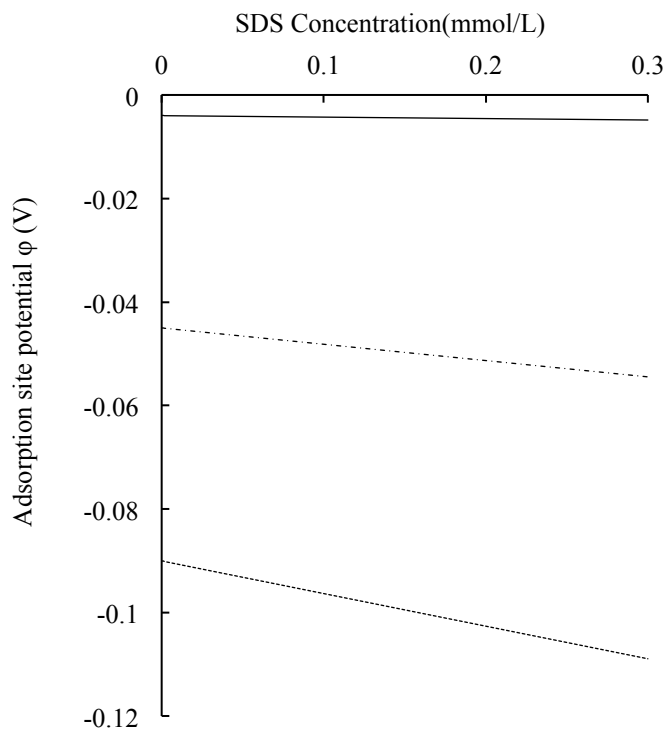


Figure 4. Calculated site potential as a function of SDS equilibrium concentration at different pH values and the same NaCl concentration of 0.1 mol/L. Lines present pH3 (—), pH5 (---) and pH7 (····).

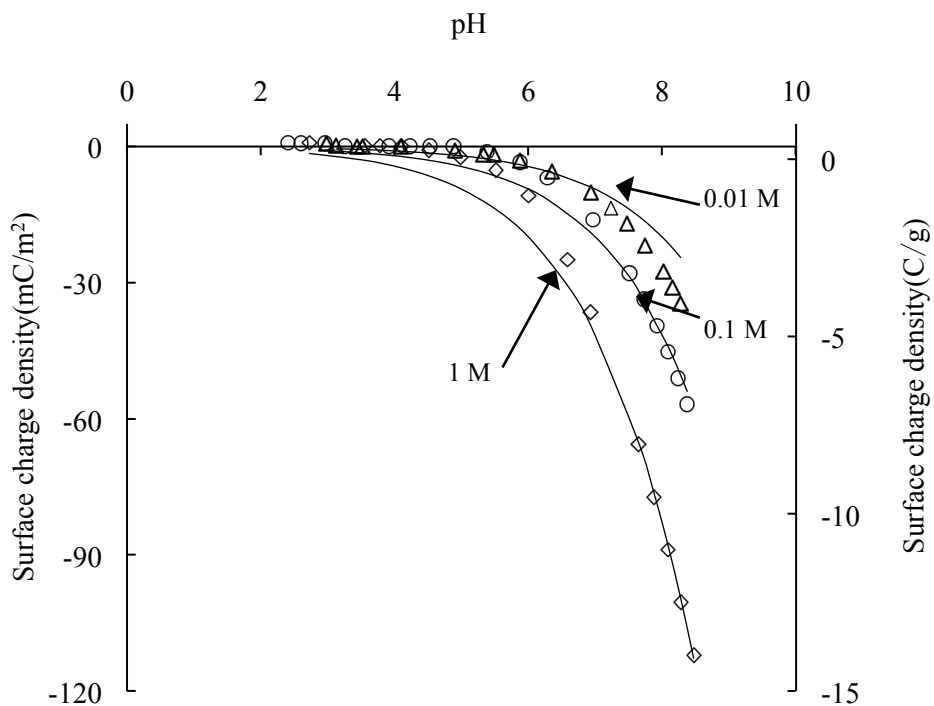


Figure 5. Surface charge density of silica. Symbols are measured values and the solid lines are calculated values by 1-pK basic Stern model.

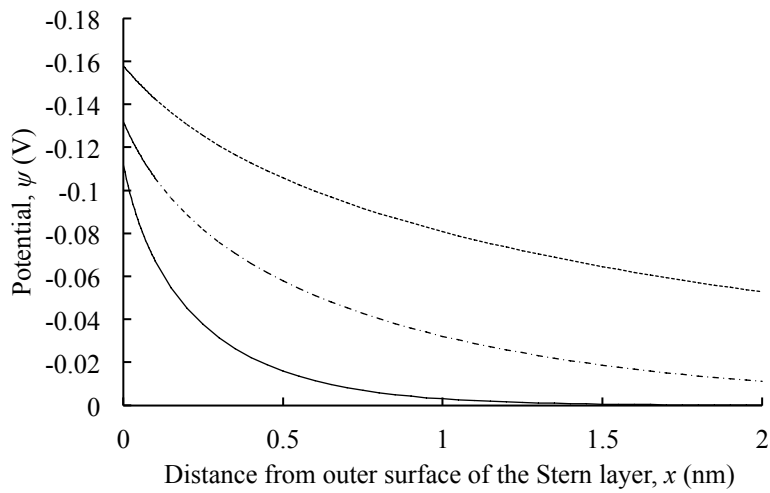


Figure 6. Calculated potential distributions near the silica surface without SDS at pH 4.5 and different NaCl concentrations.

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

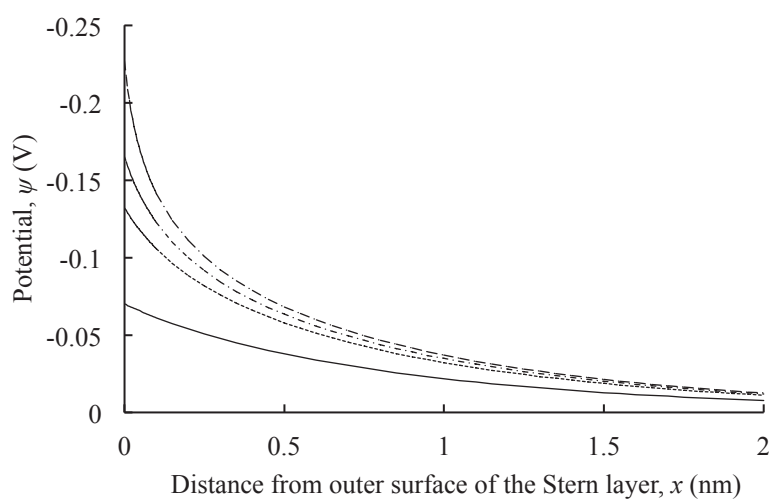


Figure 7. Calculated potential distributions near the silica surface without SDS at different pH values and the same NaCl concentration of 0.1 mol/L.

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

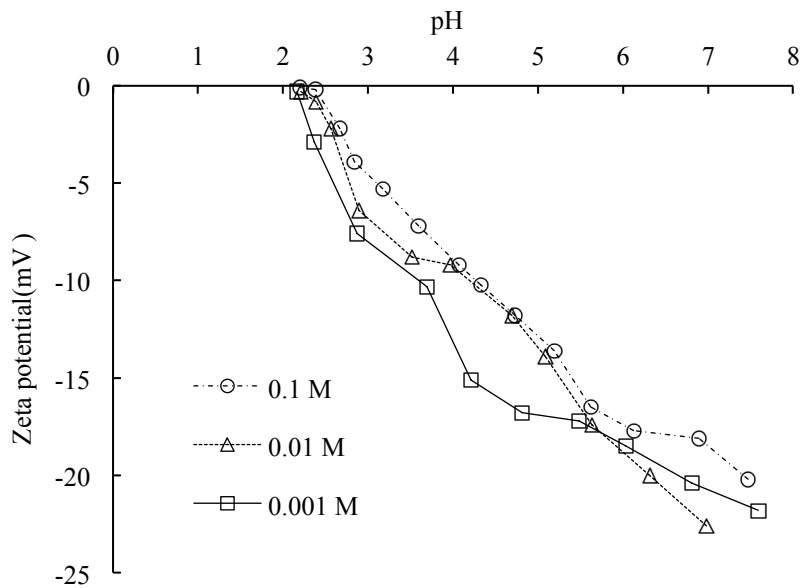


Figure 8. Zeta potential as a function of pH under different electrolyte concentrations.