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Author(s)	Ahmed, Farook; Ishiguro, Munehide
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Effect of adsorption site potential on adsorption of sodium dodecylbenzenesulfonate in highly humic volcanic ash soil

Farook AHMED¹, Munehide ISHIGURO²

¹*Graduate School of Environmental Science, Okayama University, Tsushima-naka, Okayama 700-8530, Japan and* ²*Laboratory of Soil Conservation, Research Faculty of Agriculture, Hokkaido University, Kita 9 Nishi 9, Sapporo, 060-8589 Japan*

Correspondence: M. ISHIGURO, Hokkaido University, Laboratory of Soil Conservation, Research Faculty of Agriculture, Kita 9 Nishi 9, Sapporo, 060-8589 Japan.

E-mail addresses: ishi-m@env.agr.hokudai.ac.jp

Tel. +81(11)706 2565.

farookahmed12@yahoo.com (F. Ahmed).

Present address.

¹Ministry of Public Administration, Government of Bangladesh, Dhaka-1000 in lieu of Ministry of land, Raipura, Narsingdhi, Bangladesh

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Abstract

Sodium dodecylbenzenesulfonate (DBS) is a very useful and widely used anionic surfactant. This surfactant sometimes creates environmental problems when it is released into the water environment. However, the factors influencing the adsorption of DBS in soil have not been studied well. In this study, the influence of the potential at the adsorption site on the adsorption of DBS in a soil was first elucidated by using a theoretical adsorption equation. The soil was a highly humic soil with a negative charge. The amount of DBS adsorbed was measured with a batch method for different electrolyte concentrations of NaCl at pH 4.5 and 6.5. The adsorption site potential of the soil was obtained with the modified Langmuir adsorption equation. The adsorption of DBS decreased as the electrolyte concentration decreased and as the pH increased because the repulsive electric potential between DBS and the soil increased. These results were confirmed by the obtained adsorption site potential and the measured electrophoretic mobility. The difference between the adsorption of DBS with a linear and with a branched carbon chain was also detected, and this difference was related to the free energy of micellization. Because DBS adsorption is strongly affected by electrolyte concentration and pH, these two factors must be carefully considered to predict the fate of DBS in soil and water environments.

Key words: Adsorption, anionic surfactant, electrolyte concentration, humic soil, potential.

INTRODUCTION

Sodium dodecylbenzenesulfonate (DBS) is a very common and popularly used anionic surfactant; it is used as the active ingredient of laundry detergent and as an anti-caking agent in many domestic and industrial materials, including chemical fertilizers. DBS is also popular as an emulsifying agent in agricultural chemicals because of its ability to change the physicochemical nature of surfaces. Additionally, DBS is the most common pollutant found in almost all environmental settings (McAvoy et al. 1993). Overall, DBS is used in large quantities and enters the environment primarily through wastewater and sludge.

The discharge of DBS into the environment brings DBS into contact with soil and allows DBS to adsorb onto soil. The adsorption of DBS by soils and sediments is an important process that affects the transport and toxicity of DBS (Field et al. 1992; Wolf and Feijtel 1998). Sometimes, surfactants are used in soil and groundwater remediation (Zhao et al. 2006). The adsorption of anionic surfactants in a wide concentration range needs to be investigated to understand the application of anionic surfactants to remediation of contaminated soil and groundwater (West and Harwell 1992; Allred and Brown 1996; Ko et al. 1998). Adsorption studies of cationic surfactant on humic acids have been recently conducted (Koopal et al. 2004; Yee et al. 2006; Ishiguro et al. 2007; Ishiguro and Koopal 2011). Yee et al. (2009) found that an anionic surfactant adsorbed only slightly on humic acids. Nonionic and cationic surfactants have much higher sorption with soil and sediment than anionic surfactants do (Urano et al. 1984; Rodriguez-Cruz et al. 2005; Ying 2006). It has been observed that DBS adsorption decreased as pH increased (Inoue et al. 1978; Fytianos et al. 1998; Li et al. 2008; Ahmed et al. 2012b) and that DBS adsorption correlated positively with organic matter content (McAvoy et al. 1994; Fytianos et al. 1998). The effect of pH and DBS concentration on the dissolution of humic substances from highly humic volcanic ash soil at different electrolyte concentrations has also been observed (Ahmed et al. 2012a).

Koopal et al. (1995) have studied the influence of electrolyte concentration on the adsorption of ionic surfactants onto oppositely charged metal oxide surfaces. They showed that an increase in the electrolyte concentration causes screening of the electric attraction between the surfactant and metal surface and leads to a decrease in adsorption at lower surfactant concentrations. In contrast, an increase in the electrolyte concentration enhances the adsorption of anionic surfactant onto a negatively charged solids (Nevskaia et al. 1998; Paria et al. 2005; Li et al., 2008). However, the theoretical interpretation for those phenomena has not been conducted exactly, although those for the adsorption on oppositely charged surface has been done well.

DBS with a linear carbon chain (L-DBS) is used throughout the world for domestic and commercial uses. However, some Latin American countries use DBS with a branched carbon chain (B-DBS) because B-DBS has a lower cost, even though this form of DBS is known to have detrimental effects on the environment and especially on water quality (Campos-Garcia et al. 1999). It is known that B-DBS has low biodegradability (Cain 1994). Adsorption studies in soils and alumina comparing linear and branched carbon chain structures were studied (Dick et al. 1971; Inoue et al. 1978; Ahmed et al. 2012b). However, those in negatively charged soils at different electrolyte concentration are rare.

The objective of this study was to investigate the influence of the potential at the adsorption site on DBS adsorption in a negatively charged soil by using the theoretical adsorption equation. The adsorption isotherms of both B-DBS and L-DBS were also systematically investigated. A highly humic volcanic ash soil was used in this experiment because it is a soil that contains a large amount of organic matter and especially because it is negatively charged (Ishiguro et al. 2003).

MATERIALS AND METHODS

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.

Surfactant

DBS ($\text{C}_{12}\text{H}_{25}\text{C}_6\text{H}_4\text{SO}_3\text{Na}$, molecular weight $348.48 \text{ g mol}^{-1}$) was purchased from Tokyo Kasei Kogyo Co. L-DBS (soft type DBS) and B-DBS (hard type DBS) had purities of approximately 95 % and were used without further purification.

Adsorption experiments

A batch experiment was conducted to determine the DBS adsorption isotherm of the soil and to investigate the influence of electrolyte concentration at different pH conditions (pH 4.5 and pH 6.5) at room temperature ($25 \pm 1 \text{ }^\circ\text{C}$). The soil (2.5 g dry weight basis) was placed in a 50 cm^3 centrifuge tube. The soil was equilibrated with different concentrations of electrolyte solution (1 mM, 10 mM, 100 mM and 500 mM NaCl), and the pH of the solution was adjusted to 4.5 or 6.5 with dilute HCl or NaOH. After the supernatant from the tube was discarded, 25 ml of the DBS solutions (ranging from 0.001 to 10.0 mM) at the same NaCl concentrations with that of the former equilibrated solutions were mixed with the soil and were shaken well for 24 hours. To be accurate, the Na concentrations of the DBS solutions were somewhat larger than those of the former equilibrated solutions as Na accompanied with DBS was added more to the DBS solutions, although Cl concentrations were same. Afterwards, the soil solution was centrifuged for 10 minutes at 8000 rpm. The supernatant in the tube was collected, and the surfactant concentration of the supernatant was measured with an anionic

surfactant-selective electrode (Fukui et al. 2003). The homemade 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 in the collected supernatant. The electromotive force (EMF) was measured by a digital voltmeter with high input impedance at 25 ± 1 °C. The EMF, E , can be expressed with the following equation:

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

where S is the experimental slope. The theoretical value of S is 59.2 mV at 25 °C (Nernstian slope). If the surfactant concentration was higher than the critical micelle concentration, the concentration was measured after dilution. To avoid the effects of extended exposure to the dissolved humic substances on the electrode, the electrode was carefully washed before each measurement and was always checked with a standard solution to obtain the correct result. The amount of surfactant adsorbed in the soil was obtained by subtracting the amount of DBS in the soil solution from the amount added to the soil.

Critical micelle concentration (CMC)

The CMC of DBS at different concentrations of NaCl was obtained with the anionic surfactant-selective electrode. The EMF was measured at each DBS concentration. At concentrations below the CMC, a straight calibration line (EMF as a function of the logarithm of the DBS concentration) was obtained according to equation (1). At concentrations above the CMC, the EMF became almost constant. The CMC was obtained at the bend in the calibration line (Ishiguro et al. 2007; Ishiguro & Koopal 2009).

Electrophoretic mobility measurement

The electrophoretic mobility of the soil particles was measured under the same solution conditions as the adsorption experiment (Model 502, Nihon Rufuto, Japan). To obtain a good measurement, the soil and the solution were mixed in a weight ratio of approximately 1 : 20 000. In this experiment, the large soil particles sank in the measurement cell; accordingly, the mobility of the small soil particles was measured.

Evaluation with the Langmuir-Freundlich-Hill adsorption equation

The measured adsorption isotherms were evaluated with the following Langmuir-Freundlich-Hill adsorption equations (Ishiguro & Koopal 2011):

$$q = Q \frac{(KC)^n}{1 + (KC)^n}, \quad (2)$$

$$\Delta G \text{ (J mol}^{-1}\text{)} = RT \ln K, \quad (3)$$

where q is the amount of surfactant adsorbed, Q is the maximum adsorption, K is the adsorption constant, C is the equilibrium DBS concentration (M), and n is the cooperativity or non-ideality, which indicates the deviation from the Langmuir equation in which $n = 1$. In equation (3), ΔG is the adsorption energy, R (J K⁻¹ mol⁻¹) is the gas constant, and T (K) is the absolute temperature.

The influence of the adsorption site potential, φ , can be explained by the following equation:

$$K = \kappa \exp\left(\frac{F\varphi}{RT}\right), \quad (4)$$

where κ is the intrinsic adsorption constant, and F (C mol⁻¹) is the Faraday constant. This adsorption model is adopted here because this model indicates cooperative adsorption with n and includes the adsorption site potential. The adsorption site potential can be assumed as a Donnan potential because the soil particles are covered with the charged humic substances. The n , K , κ and φ values in the equations were obtained by fitting the measured curve. The Q

value was obtained from the measured isotherm at approximately the CMC, and it was fixed at 20 mmol kg⁻¹. This value was adopted because Q is the maximum adsorption on the soil surface sites and the measured adsorptions were roughly that value at approximately the CMC where the surfactant monomer concentration became maximum. Above the CMC additional surfactant may be adsorbed as multilayer complex.

RESULTS AND DISCUSSION

Electrophoretic mobility

The measured electrophoretic mobilities are shown in Fig. 1. All the mobilities were negative because the soil has a negative charge. Therefore, the electric interaction between the soil and the negatively charged surfactant is repulsive. With increased DBS adsorption, the mobility became more negative because of the increase in the negative charge of the soil through adsorption of DBS. The absolute value of the mobility became smaller with increasing electrolyte concentration from screening of the electric field. The absolute value was larger at the higher pH value (pH 6.5), because the negative charge of the soil increased.

DBS adsorption

The DBS adsorption isotherms are shown in Fig. 2. The amount of DBS adsorbed increased as the electrolyte concentration increased for both B-DBS and L-DBS. This result is consistent with those of other studies (Nevskaia et al. 1998; Paria et al. 2005; Li et al. 2008). The increase occurred because at higher electrolyte concentrations the repulsive electric potential at the adsorption site became smaller, as shown in the next section, from screening of the electric field. This condition was also confirmed by the decrease in the absolute value of the electrophoretic mobility as the electrolyte concentration increased, mentioned in “Electrophoretic mobility” section.

For samples with the same electrolyte concentration, the amount of DBS adsorbed was larger at lower pH. This result is consistent with those of other studies (Fytianos et al. 1998; Li et al. 2008; Ahmed et al. 2012b). The result indicates that the repulsive electric potential at the adsorption site became smaller at lower pH, as will be shown in the next section, because the absolute value of the pH-dependent, negative charge of the soil was smaller at lower pH. This condition was also confirmed by the smaller absolute value of the electrophoretic mobility at lower pH, mentioned in section 3.1.

Evaluation with the Langmuir-Freundlich-Hill adsorption equation

The adsorption isotherm was divided into three parts; a part with a steep slope at the lower DBS concentrations, a part with a moderate slope at the intermediate DBS concentrations, and a part near the CMC. The adsorption isotherm at the intermediate DBS concentrations was evaluated with the theoretical adsorption equation under the assumption that $n=1$ to approximate the adsorption site potential, ϕ . The κ and ϕ values in the equations were obtained by fitting the measured curve. For example, the calculated isotherms at pH 6.5 for B-DBS are shown in Fig. 3. The obtained κ values were 1.9×10^4 for B-DBS and 5.3×10^4 for L-DBS. The obtained ϕ values are shown in Fig. 4. The calculated ϕ became straight when plotted as a function of $\log$ (DBS concentration) for convenience, as shown in Fig. 4. The absolute value of ϕ became smaller as the electrolyte concentration increased. This result clearly confirms the screening effect of the electrolyte concentration on DBS adsorption. The dash-dot line in Fig. 3 is the calculated isotherm at $\phi=0$ in which there is no electric repulsion between the soil and surfactant. The amount adsorbed decreased as the absolute value of ϕ increased because the repulsive electric potential increased. The effect of ϕ on the adsorption energy can be calculated with equations (3) and (4). The adsorption energy at $\phi=0$ at pH 6.5 for B-DBS, $\Delta G \text{ (J mol}^{-1}\text{)} = RT \log \kappa$, is $9.9RT \text{ J mol}^{-1}$. The adsorption energy decreases by $0.39RT \text{ J mol}^{-1}$ if the absolute value of ϕ increases by 10 mV.

The absolute value of φ became smaller at lower pH (Fig. 4). This decrease reflects the decrease of the negative charge of the soil. Therefore, the repulsive electric potential at the adsorption site became smaller, and the adsorption of DBS increased at lower pH. The φ values showed a similar trend to that of the electrophoretic mobilities.

A steep slope was observed in the adsorption isotherm at the lower DBS concentrations. This steep slope indicates that the surfactants are adsorbed simultaneously through lateral interactions among the hydrophobic carbon chains of the surfactants. This process is called cooperative adsorption. The cooperativity can be described by the n value in equation 2. The calculated values were $n=10$ at pH 4.5 for both B-DBS and L-DBS, $n=15$ at pH 6.5 for B-DBS, and $n=16$ at pH 6.5 for L-DBS. These values explicitly indicate strong cooperativity regardless of electrolyte concentration. Ahmed et al. (2012b) reported similar results in 100 mM NaCl. The cooperative adsorption was observed only at lower DBS concentration probably because no proper room for cooperative adsorption remained at higher DBS concentration.

Comparison between adsorption of DBS with branched and linear carbon chains

The comparison between adsorption of DBS with branched and linear carbon chains is given in Fig. 5. For the same solution conditions, the amount of L-DBS adsorbed was always higher than that of B-DBS. This result is consistent with the results obtained by other researchers where the electrolyte concentration was not changed (Dick et al. 1971; Inoue et al. 1978; Ahmed et al. 2012b). Even at different electrolyte concentration, the relation between those B-DBS and L-DBS was similar. This result indicates that the flexible linear conformation of L-DBS is more suitable for the adsorption in the complicated structure of the humic soil where the surfactants aggregated. This result also corresponds to the fact that micellization occurs at a lower CMC for the L-DBS than that for the B-DBS. The theoretical indication of these differences is that the κ value is larger for the L-DBS than it is for the B-DBS in the

non-cooperative region; κ is 5.3×10^4 for L-DBS and 1.9×10^4 for B-DBS. The intrinsic adsorption energy is obtained with equation (3); it is $10.9RT \text{ J mol}^{-1}$ for L-DBS and $9.9RT \text{ J mol}^{-1}$ for B-DBS. For comparison with the free energy of micellization, the difference per mole between the free energies of the surfactant in a micelle and in water, ΔG_{mic} , was obtained with the following equation:

$$\Delta G_{\text{mic}} = RT \ln x \quad (5)$$

where x is the mole fraction of the surfactant at CMC (Hiemenz 1986). The CMCs for DBS, ΔG_{mic} and the differences between the ΔG_{mic} for B-DBS and L-DBS are shown in Table 2. The average of differences in ΔG_{mic} is $1.3RT \text{ J mol}^{-1}$. The value is close to the difference between the intrinsic adsorption energies of L-DBS and B-DBS, $10.9RT \text{ J mol}^{-1} - 9.9RT \text{ J mol}^{-1} = 1.0RT \text{ J mol}^{-1}$. This similarity indicates that the adsorption energy is related to the free energy of micellization (i.e. hydrophobic interaction) because both energies are related to the interactions of the hydrophobic chains. Therefore, attraction between the surfactant and the soil is supposed to be the hydrophobic interaction.

CONCLUSIONS

We investigated the adsorption of DBS in highly humic soil. In particular, the influence of the repulsive electric potential on adsorption was elucidated by calculating the adsorption site potential with the modified Langmuir adsorption equation. This elucidation is the novel aspect of this study. The negatively charged surfactant, DBS, adsorbed onto the negatively charged soil through hydrophobic interactions, despite the repulsive electrostatic interaction. More surfactant was adsorbed at higher electrolyte concentrations because of the screening of the electric field at the adsorption site. More surfactant was adsorbed at lower pH conditions because of the smaller electric repulsion between the soil particles and the surfactant. These results were confirmed by the calculated adsorption site potential and the measured electrophoretic mobility. More L-DBS was adsorbed than B-DBS because of the differences

in the chain structure. The difference was related to the difference in the CMC. Cooperative adsorption was detected at lower surfactant concentrations; the n values ranged from 10 to 16, which indicated strong cooperativity. Because the adsorption of DBS is strongly affected by electric charge characteristics and because electric charge characteristics are directly related to the electrolyte concentration and pH, the electrolyte concentration and pH must be taken into careful consideration when predicting the fate of DBS in soil and water environments and especially when using this surfactant for remediation of contaminated soils.

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REFERENCES

- Ahmed F, Ishiguro M, Akae T 2012a: Dissolution of humic substances from highly humic volcanic ash soil as affected by anionic surfactant, electrolyte concentration and pH. J. Environ. Protection, 3, 280-287.
- Ahmed F, Ishiguro M, Moriguchi K, Akae T 2012b: Adsorption of sodium dodecylbenzene sulfonate on highly humic non-allophanic andisol at high-electrolyte concentration. J. Japanese Soc. Soil Phys., 123, 45-54.
- Allred B, Brown GO 1996: Anionic surfactant transport characteristics in unsaturated soil. Soil Sci., 161, 415-425.
- Cain RB 1994: Biodegradation of detergents. Curr. Opin. in Biotech., 5, 266-274.
- Campos-Garcia J, Esteve A, Vazquez-Duhalt R, Ramos JL, Soberon-Chavez G 1999: The branched-chain dodecylbenzene sulfonate degradation pathway of *Pseudomonas*

243 *aeruginosa* W51D involves a novel route for degradation of the surfactant lateral alkyl
 244 chain. *Applied Environ. Microbiol.*, 65, 3730-3734.

245 Dick SG, Fuerstenau DW, Healy TW 1971: Adsorption of alkylbenzene sulfonate surfactants
 246 at the alumina-water interface. *J. Colloid Interface Sci.*, 37, 595-602.

247 Fleld JA, Barber II LB, Thurman EM, Moore BL, Lawrence DL, Peakee DA 1992: Fate of
 248 alkylbenzene sulfonates and dialkyltetralinsulfonates in sewage-contaminated
 249 groundwater. *Environ. Sci. Technol.*, 26, 1140-1148.

250 Fukui H, Kaminaga A, Maeda T, Hayakawa K 2003: Preparation of surfactant anion-selective
 251 electrodes with different selectivity coefficients and a trial to determine each component
 252 in binary surfactant mixtures. *Anal. Chim. Acta*, 481, 221-228.

253 Fytianos K, Voudrias E, Papamichali A 1998: Behavior and fate of linear alkylbenzene
 254 sulfonate in different soils. *Chemosphere*, 36, 2742-2746.

255 Hiemenz PC 1986: *Principles of colloid and surface chemistry*. second ed. pp. 445, Marcel
 256 Dekker, New York.

257 Inoue K, Kaneko K, Yoshida M 1978: Adsorption of dodecylbenzenesulfonates by soil
 258 colloids and influence of soil colloids on their degradation. *Soil Sci Plant Nutr.*, 24, 91-
 259 102.

260 Ishiguro M, Koopal LK 2009: Binding of alkylpyridinium chloride surfactants to sodium
 261 polystyrene sulfonate. *Colloids and Surfaces A.*, 347, 69-75.

262 Ishiguro M, Koopal LK 2011. Predictive model of cationic surfactant binding to humic
 263 substances. *Colloids and Surfaces A.*, **379**, 70-78.

264 Ishiguro M, Tan W, Koopal LK 2007: Binding of cationic surfactants to humic substances.
 265 *Colloids and Surfaces A.*, 306, 29-39.

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

268 Ko SO, Schlautman MA, Carraway ER 1998: Partitioning of hydrophobic organic compounds
 269 to sorbed surfactants, 1. Experimental studies. *Environ. Sci. Technol.*, 32, 2769-2775.
 270 Koopal LK, Lee EM, Böhmer MR 1995: Adsorption of cationic and anionic surfactants on
 271 charged metal-oxide surfaces. *J. Colloid Interface Sci.*, 170, 85-97.
 272 Koopal LK, Goloub TP, Davis TA, 2004: Binding of ionic surfactants to purified humic acid.
 273 *J. Colloid Interface Sci.*, 275, 360-367.
 274 Li XX, Yang G, Gao X 2008: Sorption behavior of sodium dodecylbenzene sulfonate (SDBS)
 275 on marine sediments. *Water Air Soil Pollut.*, 194, 23-30.
 276 McAvoy DC, Eckhoff WS, Papaport RA 1993: Fate of linear alkylbenzene sulfonate in the
 277 environment. *Environ. Sci. Technol.*, 12, 977-987.
 278 McAvoy DC, Whik CE, Moore BL, Rapaport RA 1994: Chemical fate and transport in a
 279 domestic septic system: sorption and transport of anionic and cationic surfactants.
 280 *Environ. Toxicol. Chem.*, 13, 213-221.
 281 Nevskaia DM, Guerrero-Ruiz A, López-González J de D 1998: Adsorption of
 282 polyoxyethylenic nonionic and anionic surfactants from aqueous solution: effects
 283 induced by the addition of NaCl and CaCl₂. *J. Colloid Interface Sci.*, 205, 97-105.
 284 Paria S, Manohar C, Khilar KC 2005: Kinetics of adsorption of anionic, cationic, and
 285 nonionic surfactants. *Ind. Eng. Chem. Res.*, 44, 3091-3098.
 286 Rodriguez-Cruz MS, Sanchez-Martin MJ, Sanchez-Camazano M 2005: A comparative study
 287 of adsorption of an anionic and a non-ionic surfactant by soils based on
 288 physicochemical and mineralogical properties of soils. *Chemosphere*, 61, 56-64.
 289 Urano K, Saito M, Murata C 1984: Adsorption of surfactants on sediments. *Chemosphere*, 13,
 290 293-300.
 291 West CC, Harwell JH, 1992: Surfactants and subsurface remediation. *Environ. Sci. Technol.*,
 292 26, 2324-2330.

293 Wolf WD, Feijtel T 1998: Terrestrial risk assessment for linear alkylbenzenesulfonate (LAS)
 294 in sludge-amended soils. *Chemosphere*, 36, 1319-1343.

295 Yee MM, Miyajima T, Takisawa N, 2006: Evaluation of amphiphilic properties of fulvic acid
 296 and humic acid by alkylpyridinium binding study. *Colloids and Surfaces A.*, 272, 182-
 297 188.

298 Yee MM, Miyajima T, Takisawa N, 2009: Study of ionic surfactants binding to humic acid
 299 and fulvic acid by potentiometric titration and dynamic light scattering. *Colloids and*
 300 *Surfaces A.*, 347, 128-132.

301 Ying GG 2006: Fate, behavior and effects of surfactants and their degradation products in the
 302 environment. *Environ. Int.*, 32, 417-431.

303 Zhao B, Zhu L, Yang K 2006: Solubilization of DNAPLs by mixed surfactant: Reduction in
 304 partitioning losses of non-ionic surfactant. *Chemosphere*, 62, 772-779.

305

FIGURE LEGENDS

Figure 1. The effects of electrolyte concentration and pH on the electrophoretic mobility.

•○ 1 mM NaCl; ■□ 10 mM NaCl; ▲△ 100 mM NaCl; ◆◇ 500 mM NaCl.

-----pH6.5; ——pH4.5.

Figure 2. The effects of electrolyte concentration and pH on the DBS adsorption isotherms.

Figure 3. The calculated isotherms compared with the measured isotherms for B-DBS at pH 6.5. The black symbols denote the measured values. The dotted lines are the calculated values in the cooperative region, the solid lines are the calculated values in the non-cooperative region, and the dash-dot line is the calculated value if the adsorption site potential $\varphi=0$. The numbers in the figure denote the NaCl concentrations.

Figure 4. The effects of electrolyte concentration and pH on the adsorption site potential.

—— pH 4.5, - - - - - pH 6.5,

•○ 1 mM, ■□ 10 mM, ▲△ 100 mM, ◆◇ 500 mM NaCl.

Figure 5. A comparison of the adsorption isotherms for DBS with branched and linear carbon chains.