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Effect of Divalent Cationic Ions on the Adsorption Behavior of Zwitterionic Surfactant at Silica/Solution Interface

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The adsorption behavior of zwitterionic surfactant dodecyl sulfobetaine (DBS) on a silica/solution interface with Ca^{2+} , Mg^{2+} existing in aqueous solution is explored by atomistic molecular simulations. The interaction energy contribution of van der Waals and electrostatic potentials in the surfactants/water/silica system are respectively calculated, from which the electrical interaction can be found to play a decisive role in the adsorption tendency of DBS on the silica surface with or without inorganic ions, despite different mechanisms. The distinct decrease of energy has been found to be derived from electrical interaction when DBS adsorb on the silica surface covered by Ca^{2+} or Mg^{2+} . Therefore, it can be predicted that the cationic ions combined on the negatively charged silica surface in a mineral water medium might decrease the adsorption trend of DBS on the silica surface, which has been experimentally proven by TOC measurement. Structural information of the close interface layer and the distribution of water molecules are analyzed after the complete molecular dynamics simulation using a ternary model. Ca^{2+} and Mg^{2+} combined on the silica surface can reduce the adsorption amount of DBS by preventing the direct interaction between DBS and surface, and bringing about the orientation reversal of DBS molecules to break the order of adsorption interface layer. Furthermore, changes in the status of the water spreading on the silica surface caused by the complexation of cations are also an important reason in the adsorption reduction.

Introduction

The adsorption of surfactant at the solid/liquid surface plays a critical role in many technological and industrial processes, such as dispersion/flocculation, flotation, detergency and enhanced oil recovery. With the characteristic of interfacial enrichment, the solid/liquid interfacial properties could be changed effectively by surfactant, but it is not the best choice due to the stronger interfacial adsorption tendency in some cases. For instance, the appropriate adsorption of surfactants on a mineral surface can modify the key properties of the oil/solid interface to enhance oil recovery (EOR) while greatly increasing the cost by an excess adsorption.¹

The betaine-type of zwitterionic surfactant, with both positively and negatively charged hydrophilic groups in the same molecule, has many excellent properties, such as good water solubility, broad isoelectric ranges, and resistance to hard water;² accordingly it has wide potential utilization in cosmetics, health care products, pharmaceuticals, and so on. Adsorption research of some carboxybetaines on negatively charged silica surfaces has been studied since 1988,^{3–9} though it received less attention than ionic surfactants and nonionic surfactants. Its excess absorption is caused by the interaction of the positively charged groups and the negatively charged surface of the reservoir induces prevalent concern and restricts its application in practical

processes. In 1997, J. Zajac et al.^{10,11} found an amazing phenomenon that sodium ions can reduce the amount of betaine-type surfactant adsorbed at the silica surface, and the higher concentration of sodium affects more obviously on the adsorption. Recently, the betaine-type of zwitterionic surfactant has drawn great attention because of its potential application in EOR,^{12,13} especially in the high salinity oil reservoir. However, the mechanism of its high salt adaptation and the effect of divalent cationic ions on the adsorption to the silica surface are not clear, which is very conventional and important in mineral water medium.

The conduct of adsorption between the surface of the adsorbent and the adsorbed species is usually considered to be led mainly by the following aspects: (I) electrical interactions, which is a strong type, (II) hydrophobic bonding, (III) polarization of π electrons, (IV) dispersion forces, while not every system contains all four aspects,^{14–17} and the above interactions are varied by the adsorbent and the adsorbed species as well as the environment.^{18,19} Regarding the effect of salinity on the adsorption, effects of salt ions on the adsorption of traditional anionic, cationic, and nonionic surfactants to silica have been studied for many years. The inorganic salts are considered to have three modes of action generally,²⁰ and the concentrations of salt and surfactant determine the mode of action that they take as well as their types. First, a screen of salt ions decreases the Coulombic attraction between the headgroup and surface, leading to a decrease in adsorption, as Koopal et al. observed in the isotherm of anionic and cationic surfactants onto oppositely charged solid surfaces.²¹ Second, salt ions screen the repulsions between adsorbing head groups of surfactants and increase surface coverage.²² Third, the strong adsorption of

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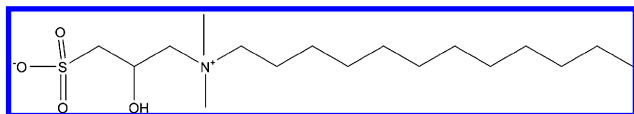


Figure 1. Surfactant used in this study.

inorganic ions on the polar surface leads to a displacement of surfactant molecules, decreasing adsorption.²³ Because there are both positively and negatively charged hydrophilic groups in the same molecule of betaine-type surfactants, the interaction between the surfactants and the solid surface is complicated, and is not easily explained by the above qualitative disciplines, especially with inorganic ions existing in the aqueous solution.

Recently, molecular simulation has been proven to be a powerful tool to study the adsorption behavior of surfactants at the solid/liquid interface. Not only coarse-grain molecular dynamics simulations of traditional anionic surfactant and nonionic surfactant molecules on a graphite surface have been performed to study their self-assembly behavior,^{24,25} but also the all atomic-level computational simulation has been performed to study the adsorption state of cationic surfactant dodecyl trimethyl ammonium bromide molecules at the graphite surface.²⁶

In this work, the effect of divalent cations Ca^{2+} and Mg^{2+} on the adsorption behavior of zwitterionic surfactant DBS (see Figure 1) on silica/solution interface was investigated by molecular dynamics simulation with binary model and complete ternary model. The interaction energies between the DBS layer and the silica surface covered by cationic ions were calculated to be corresponded to the adsorption trend at different salinity. From the detailed structural information of DBS molecules inside the interfacial phase and the distribution of water molecules which was provided by completely molecular dynamics simulation, Ca^{2+} and Mg^{2+} were found to play important role in weakening the adsorption of DBS on the silica surface by electrical mechanism beside complexation mechanism. As a validation of adsorption weaken by Ca^{2+} , total organic carbon (TOC) analyzer was employed to analyze the amount of surfactants adsorbed on the silica/solution interface.

Simulation Details. A binary model was used in our simulation as an initial step toward understanding the molecular scale direct effects between DBS and the surface adsorbed divalent cations, no water molecules were included in the system in this initial exploration.²⁷ In addition, ternary simulation model which was used for molecular dynamics simulation consists of a mineral surface, an adsorbed layer of DBS, and an aqueous layer for building a water-based system.

To generate the mineral surface, an initial lattice of silica model which is a tetrahedral, trigonal crystal system and characterized by the following lattice parameters: $a = 4.913 \text{ \AA}$, $b = 4.913 \text{ \AA}$, $c = 5.4052 \text{ \AA}$, and $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 120^\circ$, which were taken from the Material Studio structure library. A silica supercell of $7 \times 7 \times 1$ was then rebuilt without modifying its symmetry.

The high salinity was presented in view of the following two points of the actual condition: (i) the solution pH is higher than the isoelectric point of silica; (ii) the surface of hydrophilic silica was negatively charged,²⁸ and adsorbed by calcium ions and magnesium ions according to the high salinity in the solution.^{29,30} Within the distance (Debye length $1/\kappa$) from the charged surface into the solution, the major portion of the electrical interactions with the surface could occur. When the salt concentration is very high, almost all of the balanced cations adsorb on the solid/solution interface. The details about Debye length see Supporting

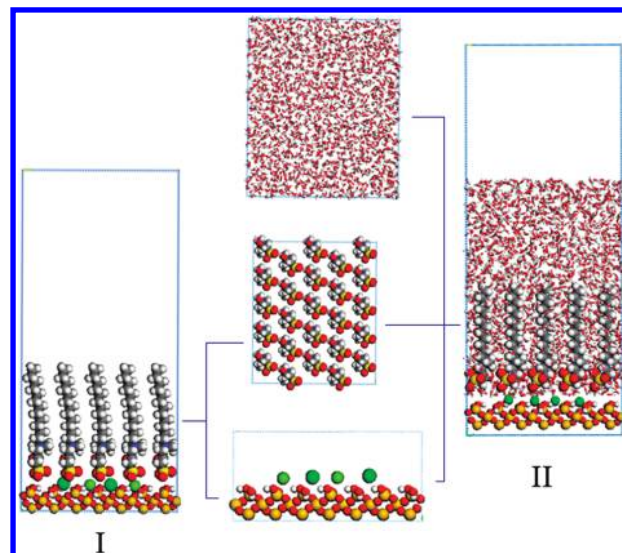


Figure 2. Preparation of initial configuration of surfactant layer adsorbed on the silica surface according to the high salinity: a surfactant layer and the mineral surface made up the model I; model II was generated by layering a surfactant layer, a mineral surface and a water phase.

Information. Accordingly, the surface of silica is composed of hydroxyl groups and oxygen anions, along with the specific number of cations (calcium ions, magnesium ions, or a mixture of both) to represent high salinity. To avoid crystal structure deformation during minimization, the silica layer without the hydroxyl groups, oxygen anions and the divalent cations were treated as rigid body by fixing all cell dimensions. As a contrast, a surface of silica which is composed of hydroxyl groups and oxygen anions without cations was constructed to represent no salinity.

The procedure to generate the hexagonal close packing adsorbed layer of DBS was similar to the literature,³¹ except with 25 molecules per periodic cell and the approximate size match the mineral cell. For the construction of the water-based systems, the flexible SPC model was chosen to represent water molecules and the 90 \AA thick slab of water (the number of water is 3600) with the same cell parameters as the surfactants cell. The rationale of the water layer thickness will be discussed in the following part. With simulation equilibrium, the interactions between each two of surfactants, mineral surface, and water decide the adsorption behavior.

Next, the surfactant layer was placed on the surface of silica to produce the initial binary model (see Figure 2I) and energy-minimized to obtain the direct interaction energy³² between the surfactant layer and the mineral surface. The parameters are given by the COMPASS force field and the functional forms used in this simulation are described as a combination of valence terms including diagonal and off-diagonal cross-coupling terms and nonbond interaction terms as same as H. Sun's work,³³ which include an LJ-9-6 function for the van der Waals (vdW) term and a Coulombic function for an electrostatic interaction, and they are used for interactions between pairs of atoms that are separated by two or more intervening atoms or those that belong to different molecules. The chemical structures and partial charges of DBS and silica are shown in Figure S2 of the Supporting Information. The strength of interaction of the surface with the adsorbate was reflected by value of this energy. The calculation is similar to adsorption energy except considering cations and solid surface as a whole part. The interaction energy $E_{\text{DBS/silica}}$ is obtained from the following equation:^{34,35}

$$E_{\text{DSB/silica}} = \frac{E_{\text{total}} - (E_{\text{DSB}} + E_{\text{surface}})}{N_{\text{DSB}}} \quad (1)$$

In which the N_{DSB} is the number of the DBS molecules, $E_{\text{DSB/silica}}$, E_{total} , E_{DSB} , and E_{surface} are the interaction energy between DBS and the silica surface, the potential energy of the energy-minimized total system, the potential energies of DBS molecules and the mineral surface adsorbed cations or not, respectively.

Finally, a ternary simulation model (see Figure 2II) was constructed by layering a silica surface with adsorbed cations Ca^{2+} and Mg^{2+} (1:1, $N_c = 16$), a surfactant layer and a water phase with a 6-nm thick vacuum slab which was used to minimize the associated error due to periodic boundary conditions, ensuring that the molecules of the middle layer were only influenced by the upper surface of the silica.^{36,37} The 3-D periodicity was thus essentially converted to a 2-D periodicity. As a comparison, another ternary simulation model was constructed to present the pure water system without cations adsorption. The COMPASS force field was used in these simulations, 1200 ps (1 ns equilibration and 200 ps data collection) of NVT MD simulation was performed at 298 K for each system, using the Verlet algorithm and an integration step of 1 fs. Temperature was controlled by the Nose thermostat.³⁹ (Q ratio = 1). The Ewald summation method³⁸ of recognized good accuracy was applied for treating both van der Waals and electrical interactions. The Ewald expression for the electrostatic energy was composed by three terms corresponds to the real-space sum, the reciprocal-space sum and the self-energy of the charge distributions produced by the introduction of the convergence function, respectively. (See eq 2) That guarantees its accuracy of the long-range force.

$$E_Q = \frac{\eta}{2} \sum_{i,j} q_i q_j \frac{\text{erfc}(a)}{a} + \frac{2\pi}{\Omega} \sum_{n \neq 0} \left(\left[\sum_i q_i \cos(h \cdot r_i) \right]^2 + \left[\sum_i q_i \sin(h \cdot r_i) \right]^2 \right) \frac{\exp(-b^2)}{h^2} - \frac{\eta}{\sqrt{\pi}} \sum_i q_i^2 \quad (2)$$

where $a = \eta |r_i - r_j - R_L|$; $r_i = Hs_i$; $h = 2\pi (H^T)^{-1} n$ (reciprocal lattice vectors); $\Omega = \det(H)$ = cell volume; and $b = h/2\eta$. All atomistic simulations (Energy minimization and MD simulations) were run in Materials Studio 4.3 by accelrys.

Materials and Experiment Methods

DBS was synthesized by our group, and the structure was determined to be the same as DBS molecules in simulation by NMR. Deionized water was used to prepare all solutions and all chemicals were of analytical grade or better. There are two kinds of solid samples, sample 1 is pure natural quartz sand, and the treatment details of sample 1 are in the Supporting Information. To obtain sample 2, sample 1 was adsorbed by calcium ions.

A TOC analyzer (Model TOC-VCPN, Shimadzu, Kyoto, Japan) was used in this study to determine the carbon amount in the liquid to reflect the concentration of DBS. For the work principles of the TOC, see the Supporting Information. The DBS adsorption amount on silica could be obtained by the DBS concentration difference before and after adsorption process.

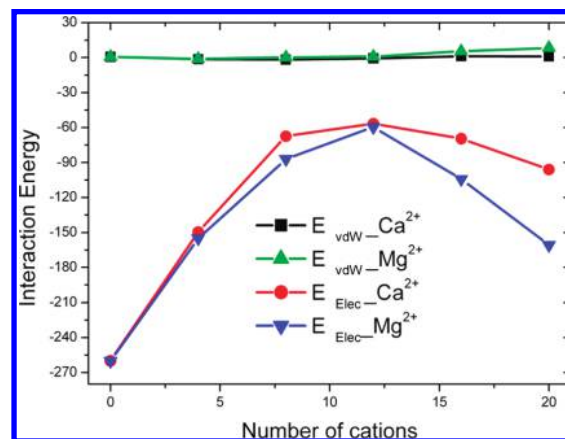


Figure 3. Total interaction energies ($E_{\text{surfactant/silica}}$) by the contribution of van der Waals (E_{vdW}) and electrostatic (E_{elec}) potentials varied with the different numbers of cations adsorbed on the silica surface.

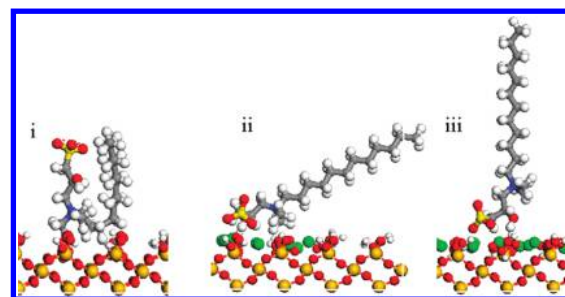


Figure 4. Three kinds of adsorption manners of DBS at pure silica surface or covered by cations.

Results and Discussion

Interaction Energy. Interaction energies were calculated to indicate the impact of divalent cations on the direct interaction between surfactant layers and the silica surface. The system is relatively more stable with greater negative energy. Total interaction energies ($E_{\text{surfactant/silica}}$) contain contributions of van der Waals (E_{vdW}) and electrostatic potentials ($E_{\text{Electrostatic}}$) which are shown separately in Figure 3. The total energy is a function of the number of cations covering the silica surface. It is noted that Electrostatic interaction plays a decisive role in the high salinity system, while the van der Waals interaction energies fluctuate in the vicinity of zero. For the nature of DBS and silica, the hydrogen bonding energy could be negligible from the total interaction energy.^{40,10}

The effects of Ca^{2+} and Mg^{2+} have been separately investigated. With the increasing of Ca^{2+} number ($N_{\text{Ca}^{2+}}$), the interaction energy increased first and then decreased, and the adsorbing mode of DBS molecule varied correspondingly. When $N_{\text{Ca}^{2+}} = 0$, the adsorption is the most stable in agreement with the most negative interfacial interaction energy between DBS and the surface. As a result, the DBS molecules are prone to adsorb on the surface of silica. The negative interaction was caused by the direct attraction between the negative charged surface and cationic part of hydrophilic group. It is very interesting to find out that the DBS molecule oriented to the solid surface by the quaternary nitrogen group getting close to the surface and the anionic group getting away from it (see figure 4, i). The $E_{\text{surfactant/silica}}$ increase with $N_{\text{Ca}^{2+}}$ increasing, and the interaction is weaker ($N_{\text{Ca}^{2+}} \geq 8$) indicating by the high value of interaction energy, which prompted the adsorption of DBS molecules was unstable comparing to the other occasions. An oblique adsorption manner of DBS molecule is shown in Figure 4ii, in which the anionic part of DBS is closer to the silica

surface as the results of the attraction between Ca^{2+} and sulfonate group of DBS, while the cationic quaternary ammonium part of DBS was attracted by the net negative charge of surface. When $N_{\text{Ca}^{2+}} \geq 12$, the $E_{\text{surfactant/silica}}$ decreased a little, but is still much higher than the value at $N_{\text{Ca}^{2+}} = 0$. According to the simulation results, the adsorption manner i and ii coexist if $N_{\text{Ca}^{2+}}$ was in the range of 0–12. The vertical manner shown in figure 4iii emerged when $N_{\text{Ca}^{2+}} \geq 16$, while ii and iii coexist if $N_{\text{Ca}^{2+}}$ was in the range of 12–16. The interaction energies summarize complex electric interactions comprising not only the repulsions between quaternary ammonium ion and Ca^{2+} , sulfonate ion and the surface of silica, which would be in positive value, but also the attractions between sulfonate ion and Ca^{2+} , sulfonate and quaternary ammonium ions belonging to different DBS molecules, which would be negative. The results can be an evidence for that Ca^{2+} play a role in weakening the adsorption of DBS on the silica surface by changing the orientation manner of surfactants accompanying the variation of the interaction energy of the system.

The effect of Mg^{2+} on the interaction energy is similar to Ca^{2+} , but the values of $E_{\text{surfactant/silica}}$ are more negative in all the coverage of Mg^{2+} than Ca^{2+} , especially when the number is more than 12, and decreased more sharply when $N_{\text{Mg}^{2+}} \geq 12$, by which it could be presumed that calcium ions play more important role than Mg^{2+} in weakening the adsorption of DBS on the silica surface.

Orientation and Distribution of DBS Molecules in the Interface Adsorption Layer. The details of interface adsorption layer of DBS on silica affected by Ca^{2+} were investigated by completed molecular dynamics simulation using ternary simulation model. S and N atoms represent negative sulfonate and positive quaternary ammonium groups, respectively. Concentration profile analysis of S and N atoms was executed by taking coordinate information as input and plotting the relative concentration in layers parallel to z axis. The distribution information and the orientation of DBS molecules on interface in pure water and in high salinity solution are presented in Figure 5, the absolute difference was particularly meaningful to understand the mechanism of the effect of cations on the adsorption behavior of the surfactants.

In Figure 5 (a), the positions of the first four corresponding peaks in the two curves are consistent, the two curves get to maximum and minimum in step, representing the orderly arrangement of positive and negative parts of the hydrophilic groups, by which the effective multiadsorbed layer of the DBS molecules was formed and its thickness is about 25 Å, see Figure 6(a). While the two curves in Figure 5(b) exhibit an inversion relationship, four major peaks of each curve show that the order lead by the electrostatic attraction of positive and negative charge groups was broken in the high salinity system, see Figure 6(b). In addition, peaks 3 and 4 in Figure 5(b) are far from peaks 1 and 2, which indicates the interaction between these DBS molecules and the solid surface are weak and desorption may take place reflecting on the decrease of the adsorption amount, then the effective adsorbed layer contains only the first two peaks only and its thickness is about 15 Å, which is thinner than that in pure water. Furthermore, the first peaks in the two curves in Figure 5(a) showed how the divalent cations affect the orientation of surfactant head groups to silica surface. In pure water, DBS oriented with the quaternary nitrogen group closing to the surface and almost all the anionic substituent group getting away except very few in the first peak attracted by positively charged group; however, the opposite orientation occurred in the high salinity solution because of the adsorption

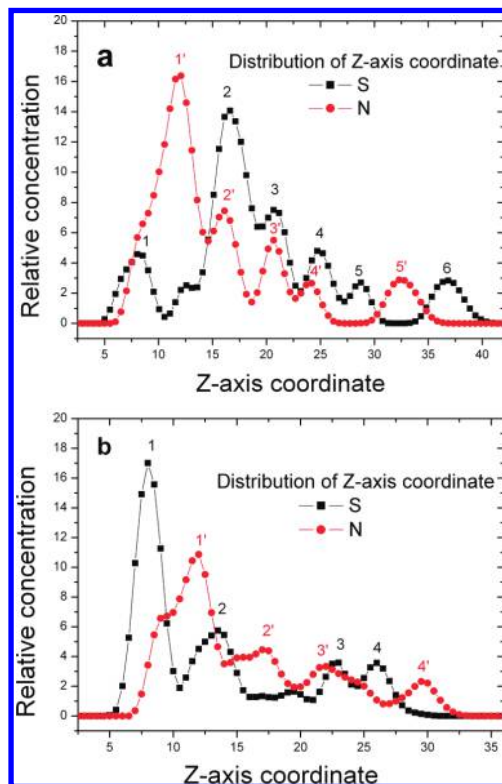


Figure 5. The distribution curve of S and N of DBS along the Z axis direction in pure water (a) and high salinity solution (b).

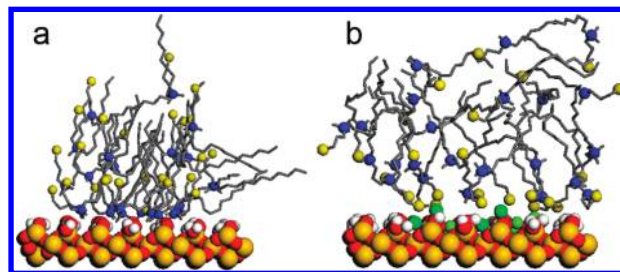


Figure 6. The schematic of electrical mechanism for adsorption reduction: (a) an orderly arrangement of DBS on silica surface caused by the attraction of positive and negative charge groups in pure water. (b) The disorderly arrangement of DBS on silica surface partly covered by cations due to the orientation reversal of DBS molecules. The effective thickness of adsorbed layer in the left is greater than the right and ordered arrangement apparently packed more tightly than the disorderly one (Top view, see Figure S3 of the Supporting Information).

of Ca^{2+} or Mg^{2+} on the solid surface, which is in accordance with the results obtained by binary model. The cations completely changed the entire adsorbed layer conformation when surface coverage became 1/3. The reversal of orientation of the surfactant head groups not only illustrated that the divalent inorganic cations on the interface layer did change the characters of the interfacial phase and it was the origin of adsorption reduction. It was worth noting that the efficiency of the conformation change of the surfactants headgroup caused by cationic ions were very high, and varied more greatly than the change of surface coverage of divalent cations on the silica surface. For the statistics details, see Supporting Information.

Simply put, the order of surfactant adsorption layer to the solid surface was thoroughly changed due to the orientation reversal of DBS molecules caused by the cations, which prevented the direct interaction between DBS and solid surface, and then broke the order of adsorption layer, which was one of

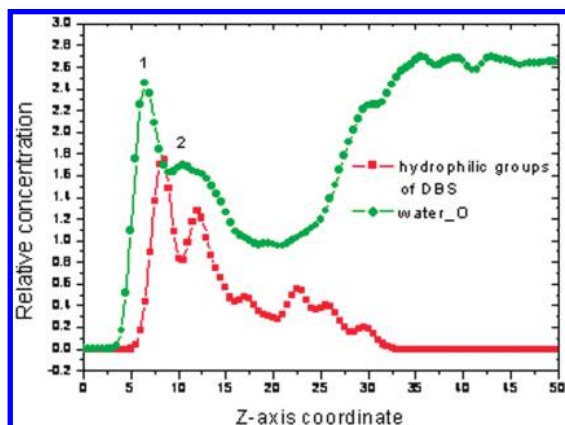


Figure 7. Concentration profile of water molecules in z axis directions is represented by the green curves. In the z -axis direction, the silica surface locates in the minimum coordinate. The interfacial region is between 3 and 25; the plateau region on the right represents the aqueous phase water. The red curve represents the concentration profile of positively and negatively charged groups in DBS.

the electrostatic mechanism of divalent cations effects for DBS adsorption reduction.

Properties of Water and Complexation Mechanism of Divalent Cations. Water molecules in the simulation presented as the combined water in interfacial phase and free water in bulk phase, which verified the correctness of the model.

TABLE 1: Statistical Analysis of Divalent Cations and DBS Molecules in the Composition of Complex

type	percentage of $\text{Ca}^{2+}/\%$	percentage of $\text{Mg}^{2+}/\%$	percentage of DBS/ $\%$
i	62.5	12.5	28
ii	37.5	87.5	72

Concentration profiles in z axis direction of water molecules were analyzed to observe the distribution of the water molecules and reflect the structure information of the DBS interface layer. There were two peaks (1 and 2) in the interfacial region (see Figure 7). Peak 1 indicated the sum of hydration bonding water molecule of solid surface, divalent cations,⁴¹ and hydrophilic groups of DBS. While Peak 2 was from the distribution of hydration bonding water molecules of quaternary ammonium and sulfonate ions in the multilayer. The plateau of the green curve represents the free water molecules in bulk phase.

According to the detailed information (see Figure 8) of interface layer provided by molecular simulation, complexation might be another mechanism for adsorption reduction of DBS caused by divalent cations. The silica surface was partially covered by divalent cations ($\text{Ca}^{2+}:\text{Mg}^{2+} = 1:1$) and the composition of the complex surrounding the divalent cations within 3 Å were found to be in two categories: (i) the octahedral complexation^{42,43} of divalent cation was generated by the participation of sulfonate group, water molecule, and atom O in $[\text{SiO}^-]$ or $[\text{SiOH}]$ of the surface. (ii) Only water molecules

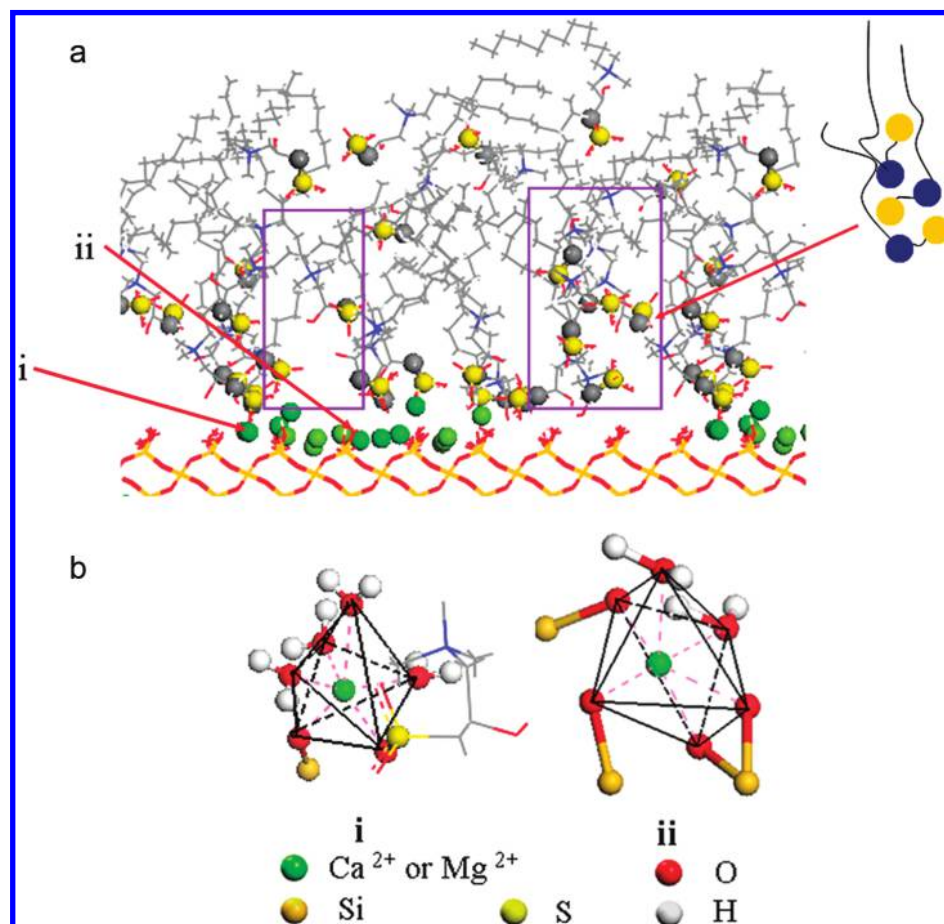


Figure 8. (a) Snapshot of side elevation of DBS adsorbed layer. Left purple rectangular box shows the low-density adsorption multilayer affected by Ca^{2+} and Mg^{2+} , while the right one denotes the representative without them. Divalent cations are divided into two kinds, i and ii. (b) Two types of cation complexation approaches. (i) Atoms O of sulfonate group, water molecule and in $[\text{SiO}^-]$ or $[\text{SiOH}]$ of the surface compose the octahedral complexation. (ii) Only atoms O of H_2O and $[\text{SiO}^-]$ or $[\text{SiOH}]$ of the surface are involved in the complexation. The atoms are colored as follows: Ca^{2+} or Mg^{2+} , green; O, red; Si, Orange; S, yellow; and H, white.

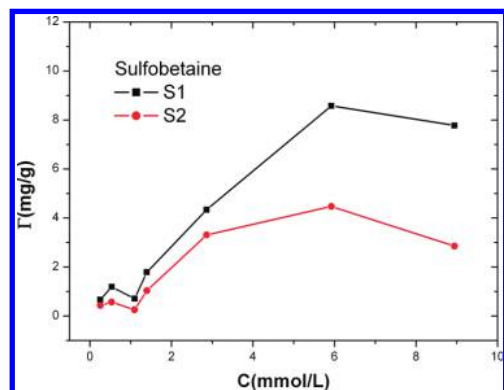


Figure 9. Adsorption isotherms of DBS on different silica surface. S1, pure silica sand; S2, silica sand covered by Ca^{2+}

and atom O in $[\text{SiO}^-]$ or $[\text{SiOH}]$ of the surface were involved in the complexation. According to the accumulation results listed in Table 1, 62.5% Ca^{2+} involved in type i, while most Mg^{2+} evolved in type ii. Compared with Mg^{2+} , Ca^{2+} has a stronger ability to form a chelate with DBS as its stronger electrical interactions, thus orientation reversal was mostly caused by Ca^{2+} . Meanwhile, Mg^{2+} was prone to complex with water and $[\text{SiO}^-]$ or $[\text{SiOH}]$ on the surface to prevent the adsorption of DBS. In total, 28% of the DBS was involved in the complex type i and 72% in type ii, and it is doubtless that the compact multilayer adsorption of DBS, like that in pure water, shown on the right purple rectangular box in Figure 8, would not happen with Ca^{2+} or Mg^{2+} existing.

Experimental Results. In the Figure 9, adsorption isotherms of DBS were measured by TOC analyzer. The results showed that the adsorption of DBS on the silica surface was small and the presences of Ca^{2+} do reduce the absorption, which verified the simulation results above.

Conclusions

Atomic-level computational simulations were built to predict and understand the adsorption behavior of zwitterionic surfactant DBS on the silica/liquid interface involving divalent cations. The simulation contained two parts: an initial step toward studying direct interaction from the binary models and adsorption dynamics of DBS on the silica surface adsorbing divalent cations. An effective route was built to predict the adsorption trends of DBS on different solid surface through evaluating the interaction energy and it can be extended to other system with different surfactants. The adsorption of zwitterionic surfactant DBS on silica was very easily run and stable without a salt being present, while adsorption on the silica surface was unstable with Ca^{2+} or Mg^{2+} , because of the high interaction energy. Ca^{2+} plays a more important role in weakening the adsorption of DBS on the silica surface than Mg^{2+} by electrical mechanism of bringing up the orientation reversal of DBS molecules and then breaking the order of adsorption layer. Mg^{2+} did better than Ca^{2+} in complexing water to prevent the direct interaction between the DBS and surface. The adsorption of DBS was apparently weakened by divalent cationic ions, and the experimental results agree well with the molecular simulation prediction.

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Supporting Information Available: The details about Debye length; the chemical structures and partial charges of DBS and silica (shown in Figure S2); the treatment details of sample 1; the work principles of the TOC; the statistics details; and the top view of Figure 6, (Figure S3). This information is available free of charge via the Internet at <http://pubs.acs.org>

References and Notes

- (1) Zhang, R.; Somasundaran, P. Advances in Adsorption of Surfactants and their Mixtures at Solid/Solution Interfaces. *Adv. Colloid Interface Sci.* **2006**, *123–126*, 213–229.
- (2) Danov, K. D.; Kralchevska, S. D.; Kralchevsky, P. A.; Ananthapadmanabhan, K. P.; Lips, A. Mixed Solutions of Anionic and Zwitterionic Surfactant (Betaine): Surface-Tension Isotherms, Adsorption, and Relaxation Kinetics. *Langmuir* **2004**, *20*, 5445–5453.
- (3) Brode, P. F. III. Adsorption of Ultra-Long-Chain Zwitterionic Surfactants on a Polar Solid. *Langmuir* **1988**, *4*, 176–180.
- (4) Partyka, S.; Lindheimer, M.; Faucompre, B. Aggregate Formation at the Solid-Liquid Interface: The Calorimetric Evidence. *Colloids Surf. A* **1993**, *76*, 267–281.
- (5) Chorro, M.; Kamenka, N.; Faucompre, B.; Partyka, S.; Lindheimer, M.; Zana, R. Micellization and Adsorption of a Zwitterionic Surfactant: *N*-dodecyl Betaine Effect of Salt. *Colloids Surf. A* **1996**, *110*, 249–261.
- (6) Liu, J. F.; Min, G.; Ducker, W. A. AFM Study of Adsorption of Cationic Surfactants and Cationic Polyelectrolytes at the Silica–Water Interface. *Langmuir* **2001**, *17*, 4895–4903.
- (7) Atkin, R.; Craig, V. S. J.; Wanless, E. J.; Biggs, S. Mechanism of Cationic Surfactant Adsorption at the Solid-Aqueous Interface. *Adv. Colloid Interface Sci.* **2003**, *103*, 219–304.
- (8) Somasundaran, P.; Krishnakumar, S. Adsorption of Surfactants and Polymers at the Solid–Liquid Interface. *Colloids Surf. A* **1997**, *123–124*, 491–513.
- (9) Paria, S.; Manohar, C.; Khilar, K. C. Kinetics of Adsorption of Anionic, Cationic, and Nonionic Surfactants. *Ind. Eng. Chem. Res.* **2005**, *44*, 3091–3098.
- (10) Zajac, J.; Chorro, C.; Lindheimer, M.; Partyka, S. Thermodynamics of Micellization and Adsorption of Zwitterionic Surfactants in Aqueous Media. *Langmuir* **1997**, *13*, 1486–1495.
- (11) Mulqueen, M.; Blankschtein, D. Prediction of Equilibrium Surface Tension and Surface Adsorption of Aqueous Surfactant Mixtures Containing Zwitterionic Surfactants. *Langmuir* **2000**, *16*, 7640–7654.
- (12) Hou, J. R.; Liu, Z. C.; Zhang, S. F.; Yue, X. A.; Yang, J. Z. The Role of Viscoelasticity of Alkali/Surfactant/Polymer Solutions in Enhanced Oil Recovery. *J. Petrol. Sci. Eng.* **2005**, 219–235.
- (13) Wang, G.; Wang, D. M.; Xia, H. F.; Ju, Y.; Liu, C. D. Mechanism for Enhancing Oil-Displacement Efficiency by Betaine Surfactant after Polymer Flooding. *Acta Petrol. Sin.* **2007**, *28*, 86–90.
- (14) Somasundaran, P.; Huang, L. Adsorption/Ggregation of Surfactants and their Mixtures at Solid–Liquid Interfaces. *Adv. Colloid Interface Sci.* **2000**, *88*, 179–208.
- (15) Goldsipe, A.; Blankschtein, D. Molecular-Thermodynamic Theory of Micellization of Multicomponent Surfactant Mixtures: 2. pH-Sensitive Surfactants. *Langmuir* **2007**, *23*, 5953–5962.
- (16) Zhou, Z. A.; Hussein, H.; Xu, Z. H. Interaction of Ionic Species and Fine Solids with a Low Energy Hydrophobic Surface from Contact Angle Measurement. *J. Colloid Interface Sci.* **1998**, *204*, 342–349.
- (17) Honciuc, A.; Baptiste, D. J.; Schwartz, K. D. Hydrophobic Interaction Microscopy: Mapping the Solid/Liquid Interface Using Amphiphilic Probe Molecules. *Langmuir* **2009**, *25*, 4339–4342.
- (18) Lu, S. H.; Bian, Y.; Zhang, L.; Somasundaran, P. pH Dependence of Adsorption of *n*-dodecyl- β -D-maltoside on Solids. *J. Colloid Interface Sci.* **2007**, *316*, 310–316.
- (19) Paria, S.; Khilar, K. C. A Review on Experimental Studies of Surfactant Adsorption at the Hydrophilic Solid–Water Interface. *Adv. Colloid Interface Sci.* **2004**, *110*, 75–95.
- (20) Hansupalak, N.; Santore, M. M. Sharp Polyelectrolyte Adsorption Cutoff Induced by a Monovalent Salt. *Langmuir* **2003**, *19*, 7423–7426.
- (21) Koopal, L. K.; Lee, E. M.; Böhrer, M. R. Adsorption of Cationic and Anionic Surfactants on Charged Metal Oxide Surfaces. *J. Colloid Interface Sci.* **1995**, *170*, 85–97.
- (22) Paria, S.; Manohar, C.; Khilar, K. C. Studies on Adsorption of Surfactants onto Cellulosic Surface and its Relevance to Detergency. *JIES Chem. Eng.* **2003**, *43*, 34–44.
- (23) Nevskaja, D. M.; Guerrero-Ruiz, A.; López-González, J. de D. Adsorption of Polyoxyethylene Nonionic and Anionic Surfactants from Aqueous Solution: Effects Induced by the Addition of NaCl and CaCl_2 . *J. Colloid Interface Sci.* **1998**, *205*, 97–105.
- (24) Hector, D. Self-Aggregation of the SDS Surfactant at a Solid-Liquid Interface. *J. Phys. Chem. B* **2007**, *102*, 4054–4059.

- (25) Srinivas, G.; Nielsen, S. O.; Moore, P. B.; Klein, M. L. Molecular Dynamics Simulations of Surfactant Self-Organization at a Solid Liquid Interface. *J. Am. Chem. Soc.* **2006**, *128*, 848–853.
- (26) Du, H.; Miller, J. D. Adsorption States of Amphipatic Solutes at the Surface of Naturally Hydrophobic Minerals: A Molecular Dynamics Simulation Study. *Langmuir* **2007**, *23*, 11587–11596.
- (27) Sanchez, F.; Zhang, L. Molecular Dynamics Modeling of the Interface between Surface Functionalized Graphitic Structures and Calcium-Silicate-Hydrate: Interaction Energies, Structure, and Dynamics. *J. Colloid Interface Sci.* **2008**, *323*, 349–358.
- (28) Ller, R. K.; Aler, R. K. *The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties and Biochemistry of Silica*; Wiley: New York, 1979.
- (29) Santanu, P.; Khilar, K. C. A Review on Experimental Studies of Surfactant Adsorption at the Hydrophilic Solid-Water Interface. *Adv. Colloid Interface Sci.* **2004**, *110*, 75–95.
- (30) Dishon, M.; Zohar, O.; SiVan, U. From Repulsion to Attraction and Back to Repulsion: The Effect of NaCl, KCl, and CsCl on the Force between Silica Surfaces in Aqueous Solution. *Langmuir* **2009**, *25*, 2831–2836.
- (31) Jang, S. S.; Goddard, W. A. III. Structures and Properties of Newton Black Films Characterized Using Molecular Dynamics Simulations. *J. Phys. Chem. B* **2006**, *110*, 7992–8001.
- (32) Shafir, A.; Andelman, D. Polyelectrolyte adsorption: Chemical and electrostatic interactions. *Phys. Rev. E: Stat. Phys., Plasmas, Fluids.* **2004**, *70*, 061804.
- (33) Sun, H. COMPASS: An ab Initio Force-Field Optimized for Condensed-Phase Applications - Overview with Details on Alkane and Benzene Compounds. *J. Phys. Chem. B* **1998**, *102*, 7338–7364.
- (34) Timothy, G. C.; Nora, H. L. A Computer Modeling Study of the Competitive Adsorption of Water and Organic Surfactants at Surfaces of the Mineral Scheelite. *Langmuir* **2004**, *20*, 3984–3994.
- (35) Nora, H. L.; Timothy, G. C. A Computer Modeling Study of the Inhibiting Effect of Organic Adsorbates on Calcite Crystal Growth. *Cryst. Growth Des.* **2004**, *4*, 123–133.
- (36) Andreas, K.; Selma, H. Molecular Dynamics Simulations of the Adsorption of Industrial Relevant Silane Molecules at a Zinc Oxide Surface. *J. Chem. Phys.* **2003**, *119*, 9719–9728.
- (37) Kornherr, A.; et al. Interaction of Adsorbed Organosilanes with Polar Zinc Oxide Surfaces: A Molecular Dynamics Study Comparing Two Models for the Metal Oxide Surface. *Chem. Phys. Lett.* **2004**, *393*, 107–111.
- (38) Ewald, P. Die Berechnung Optischer und Elektrostatisher Gitterpotentiale. *Ann. Phys.* **1921**, *369*, 253–287.
- (39) Nose, S. Constant Temperature Molecular Dynamics Methods. *Prog. Theor. Phys. Suppl.* **1991**, *103*, 1–46.
- (40) Rosen, M. J. *Surfactants and Interfacial Phenomena*, 3rd ed.; John Wiley & Sons, Inc.: New York, 2004.
- (41) Shao, Q.; Zhou, J.; et al. Anomalous Hydration Shell Order of Na⁺ and K⁺ inside Carbon Nanotubes. *Nano Lett.* **2009**, *9*, 989–994.
- (42) Larentzos, J. P.; Criscenti, L. J. A Molecular Dynamics Study of Alkaline Earth Metal-Chloride Complexation in Aqueous Solution. *J. Phys. Chem. B* **2008**, *112*, 14243–14250.
- (43) Netz, R. R.; Joanny, J. F. Complexation Behavior of Polyampholytes and Charged Objects. *Macromolecules* **1998**, *31*, 5123–5141.
- (44) Bisutti, I.; Hilke, I.; Raessler, M. Determination of Total Organiccarbon—An Overview of Current Methods. *Trends Anal. Chem.* **2004**, *23*, 10–11.
- (45) Hong, Y.; Li, Q. F.; Yu, J. Z. Comparison of Two Methods for the Determination of Water-Soluble Organic Carbon in Atmospheric Particles. *Atmos. Environ.* **2003**, *37*, 865–870.

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