# Adsorption and Self-Assembly of Surfactant/Supercritical CO<sub>2</sub> Systems in Confined Pores: A Molecular Dynamics Simulation

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A coarse-grained molecular dynamics simulation has been carried out to study the adsorption and self-organization for a model surfactant/supercritical CO<sub>2</sub> system confined in the slit-shape nanopores with amorphous silica-like surfaces. The solid surfaces were designed to be CO<sub>2</sub>-philic and CO<sub>2</sub>-phobic, respectively. For the CO<sub>2</sub>-philic surface, obviously surface adsorption is observed for the surfactant molecules. The various energy profiles were used to monitor the lengthy dynamics process of the adsorption and self-assembly for surfactant micelles or monomers in the confined spaces. The equilibrium properties, including the morphologies and micelle-size distributions of absorbed surfactants, were evaluated based on the equilibrium trajectory data. The interaction between the surfactant and the surface produces an obvious effect on the dynamics rate of surfactants. However, for the CO<sub>2</sub>-phobic surfaces, there are scarcely adsorption layers of surfactant molecules, meaning that the CO<sub>2</sub>-phobic surface repels the surfactant molecules. It seems to conclude that the CO<sub>2</sub> solvent depletion near the interfaces determines the surface repellence to the surfactant molecules. The effect of the CO<sub>2</sub>-phobic surface confinement on the surfactant micelle structure in the supercritical CO<sub>2</sub> has also been discussed. In summary, this study on the microscopic behaviors of surfactant/Sc-CO<sub>2</sub> in confined pores will help to shed light on the surfactant self-assembly from the Sc-CO<sub>2</sub> fluid phase onto solid surfaces and nanoporous media.

### I. Introduction

Supercritical carbon dioxide (Sc–CO<sub>2</sub>) has long been considered a promising alternative to conventional solvents.<sup>1</sup> However, several important classes of substances, such as water, ions, biomolecules, and most polymers are almost insolvable in the Sc–CO<sub>2</sub> fluid due to its low dielectric constant and polarizibility.<sup>2</sup> The solvent properties of Sc–CO<sub>2</sub> could be significantly improved by incorporation of surfactants, which may form the so-called reversed micelle in the Sc–CO<sub>2</sub> continuous phase.<sup>3,4</sup> A great deal of research effort has been devoted to design and synthesize the CO<sub>2</sub>-compatible surfactants, which contain both CO<sub>2</sub>-phobic and CO<sub>2</sub>-philic portions.<sup>5–8</sup> At present, the surfactant/Sc–CO<sub>2</sub> system has been found in a wide variety applications from the conventional chemical industry to advanced materials preparation processes.<sup>4,9,10</sup>

Among these applications, the surfactant/Sc-CO<sub>2</sub> systems at porous media or solid-liquid interfaces are increasingly employed in nanoparticle preparation,<sup>11,12</sup> polymer synthesis,<sup>13</sup> the im-

pregnation of additives,14 porous material modification,15,16 and pollutant cleaning or metal ion extraction and so forth.<sup>17-20</sup> In these regards, the Sc-CO<sub>2</sub> fluid possesses high transfer properties and zero surface tension, allowing a rapid diffusion into the inner porous solid structure and a complete wetting of the solid surface. Addition of the reversed micelle structure of surfactant molecules to the Sc-CO<sub>2</sub> fluid has not only been used to enhance transfer of CO2-insoluble substances into the porous media but also to help deposition of surfactant molecules on porous solid surfaces, which will provide a technique for surface modification. For example, the water-in-CO<sub>2</sub> microemulsion has been used to extract the metal ion in various porous solid media,<sup>18</sup> where the water nanodroplet, ranging from 1 to 10 nm, could be carried into the porous solid surfaces by the supercritical CO<sub>2</sub> fluid phases, allowing a rapid extraction of metal ions in a special manner that is not achievable with aqueous solution. Moreover, the surfactant/  $Sc-CO_2$  system has also be applied in the chemical mechanical tailoring of porous silica with a pressure tunable self-assembly process.15,16

An understanding of the micelle microstructure at solid—liquid interfaces is helpful to develop and optimize the performance in emerging and mature applications of supercritical fluid technol-

(14) Liu, H.; Yates, M. Z. Langmuir 2003, 9, 1106-1113.

- (15) Ghosh. K.; Vyas, S. M.; Lehmler, H. J.; Rankin, S. E.; Knutson, B. L. J. Phys. Chem. B 2007, 111, 363–370.
- (16) Hanrahan, J. P.; Copley, M. P.; Ryan, K. M.; Morris, M. A.; Spalding, T. R.; Holmes, J. D. *Chem. Mater.* **2004**, *16*, 424.
- (17) Huang, Z.; Luan, D. Y.; Shen, S. C.; Hidajat, K.; Kawi, S. J. Supercrit. Fluids **2005**, *35*, 40–48.
- (18) Campbell, M. L.; Apodaca, D. L.; Yates, M. Z.; McCleskey, T. M.; Birnbaum, E. R. *Langmuir* **2001**, *17*, 5458–5463.
- (19) Keagy, J. A.; Zhang, X.; Johnston, K. P.; Bush, E.; Weber, F.; Wolf, P. J.; Rhoad, T. J. Supercrit. Fluids 2006, 277.
- (20) Zhang, X.; Pham, J. Q.; Ryza, N.; Green, P. F.; Johnston, K. P. J. Vac. Sci. Technol. B 2004, 22, 818.

<sup>\*</sup> To whom correspondence should be addressed.

<sup>(1)</sup> Taylor, D. K.; Keiper, J. S.; DeSimone, J. M. Ind. Eng. Chem. Res. 2002, 41, 4451-4459.

 <sup>(2)</sup> Consan, K. A.; Smith, R. D. J. Supercrit. Fluids. 1990, 3, 51–65.
 (3) Goetheer, E. L. V.; Vorstman, M. A. G.; Keurentjes, J. T. F. Chem. Eng.

<sup>(1)</sup> Moenice 1, E. E. V., Volstman, W. A. G., Keurenges, J. T. P. Chem. Eng Sci. 1999, 54, 1589–1596.

<sup>(4)</sup> Mcclain, J. B.; Betts, D. E.; Canelas, D. A.; Samulski, E. T. Science 1996, 274, 2049.

<sup>(5)</sup> DeSimone, J. M.; Maury, E. E.; Menceloglu, Y. Z.; McClain, J. B.; Romack, T. j.; Combes, J. R. *Science* **1994**, *265*, 356–359.

<sup>(6)</sup> hoefling, T. A.; Enicj, R. M.; Beckman, E. J. J. Phys. Chem. **1991**, *95*, 7127.

<sup>(7)</sup> da Rocha, S. R. P.; Harrison, K. L.; Johnston, K. P. *Langmuir* **1999**, *15*, 419.

<sup>(8)</sup> Eastoe, J.; Paul, A.; Nave, S.; Steytler, D. C.; Robinson, B. H.; Rumsey, E.; Thorpe, M.; Heenan, R. K. J. Am. Chem. Soc. **2001**, *123*, 988–989.

<sup>(9)</sup> Eastoe, J.; Dupont, A.; Steytler, D. C. Curr. Opin. Colloid Interface Sci. 2003, 8, 267.

<sup>(10)</sup> DeSimone, J, M.; Keiper, J. S. Curr. Opin. Colloid Interface Sci. 2001, 5, 333-341.

<sup>(11)</sup> Liu, J.; Ikushima, Y.; Shervani, Z. Curr. Opin. Colloid Interface Sci. 2003, 255-261.

<sup>(12)</sup> Yu, K. M. K.; Steele, A. M.; Zhu, J.; Fu, Q.; Tsang, S. C. J. Mater. Chem. 2003, 13, 130–134.

<sup>(13)</sup> Butler, R.; Hopkinson, I.; Cooper, A. I. J. Am. Chem. Soc. 2003, 125, 14473-14481.

ogy,<sup>15</sup> which is also of great benefit to design new surfactants applied in the  $Sc-CO_2$  fluid. Furthermore, the detailed dynamics process of surfactant self-assembly in restrained pore spaces is very vital in analyzing the interaction mechanisms. There is a relatively vast amount of research on adsorption of surfactant from aqueous media onto solid surfaces by using various experimental techniques.<sup>21</sup> The previous experimental studies have revealed that surfactants absorbed on solid-liquid interfaces form the aggregates in a variety of morphologies, which are different from those in bulk phases. However, for the supercritical  $CO_2$  solution, a molecule level recognition of the morphology and structure of surfactant micelles on solid interfaces is quite inadequate. Additionally, no research has been reported, to our best knowledge, for the dynamics information of the structure transition and adsorption transfer of the micelle on solid-liquid interfaces, because very few experimental techniques can directly probe these kinetics behaviors.<sup>22</sup> Also, unlike aqueous solutions under atmospheric conditions, the experimental study on the self-assembly behavior of surfactants in supercritical fluid is relatively difficult to handle, especially in confined nanospaces.

Computer simulation can provide a microscopic level picture of such phenomena. Relatively extensive simulation studies on the surfactant/CO<sub>2</sub> in bulk phase have been conducted. For instance, the water-in-CO2 miroemulsion has been simulated for different surfactants to study the self-assembly<sup>23</sup> and structure properties<sup>24,25</sup> of the reversed micelles. The phase behaviors of model surfactants in Sc-CO<sub>2</sub> solution have been studied through evaluating the equilibrium properties, including the aggregate size distribution (ASD) and the critical micelle concentration (CMC). Scanu et al.<sup>26</sup> performed a lattice Monte Carlo simulation to explore the influence of varying nonionic surfactant concentration and CO<sub>2</sub> fluid density on the micellization and phase equilibrium of surfactant/Sc-CO<sub>2</sub> systems. They successfully reproduced the experimental trend that increasing the CO<sub>2</sub> density results in a rise in the CMC and a decrease in the micelle size. The phase diagram presented in their study<sup>26</sup> was qualitatively consistent with experimental phase diagrams for nonionic surfactants. Li et al.<sup>27</sup> also applied the discontinuous molecular dynamics simulations on model surfactant/solvent (Sc-CO<sub>2</sub>) systems to explore the effect of the surfactant volume fraction, packing fraction, and temperature on the phase behavior.

Presently, the molecular simulation study on the amphiphilic structure behavior on solid-liquid interfaces is usually limited to the aqueous systems. In the previous simulations for the aqueous solution media, it has been established that the interaction between surfactant solution and solid surfaces is the key factor in determining the interfacial reassembly behaviors. The lattice Monte Carlo (MC) simulation and molecular dynamic (MD) simulation based on coarse-grained (CG) models have been successfully used to study the various performances of surfactant on the hydrophilic and hydrophobic solid interfaces.<sup>22,28–32</sup>

A.; Rabinovich, Y.; Shah, D. O.; Moudgil, B. M. *Langmuir* 2000, *16*, 7255.
 (22) Shah, K.; Chiu, P.; Jain, M.; Fortes, J.; Moudgil, B.; Sinnott, S. *Langmuir* 2005, *21*, 5337–5342.

(26) Scanu, L. F.; Gubbins, K. E.; Hall, C. K. Langmuir 2004, 20, 514–523.
 (27) Li, Zh.; Hall, C. K. Langmuir 2004, 20, 8559–8568.

Wiljmas<sup>30</sup> studied the aggregation and adsorption of surfactants on hydrophilic surfaces by using a coarse-grained MC simulation. They found that discrete aggregates were formed on the surfaces. A MD simulation has been conducted by Shah et al.<sup>22</sup> for the mechanical properties of absorbed micelles at the liquid-silica interface. The simulation indicated that the self-aggregated surfactant structures formed spherical or elliptical shapes. In addition, fully atomistic MD simulations<sup>31</sup> were also used to study self-assembly phenomena on the surface. However, the simulation was restricted by system size and simulation time, since the MD simulation with the atomistic model needs a very long time to access the detailed structure and dynamics behavior of surfactant micelle in confined spaces. Recently Srinivas et al.29 studied the adsorption of nonionic surfactants onto a graphite surface using the MD simulation with self-developed CG models. They observed that the morphology of aggregated surfactants is dependent on the alkyl chain length, and the simulation result is in good agreement with experimental observation.

For the surfactant/Sc-CO<sub>2</sub> system in the confined porous spaces, the microscopic behaviors of surfactant are balanced by interplay of the surface interaction and the solvation effect of the CO2 solvent. As a consequence, the restricted dynamics behavior of the surfactant/Sc-CO<sub>2</sub> system may combine the different mechanisms, including the monomer/aggregate diffusion and micelle structure rearrangement. In addition, it is very interesting to recognize how the surfactant self-assembly is influenced by the presence of various solid surfaces, such as CO<sub>2</sub>-philic and CO<sub>2</sub>-phobic surfaces. Nevertheless, the detailed mechanisms of the microscopic behavior of surfactant/Sc-CO<sub>2</sub> in confined space or at solid-liquid interfaces still remain unclear. The molecular dynamics study on the microscopic behaviors of surfactant/Sc- $CO_2$  in confined pores will help to shed light on the surfactant self-assembly from the Sc-CO<sub>2</sub> fluid phase onto solid surfaces and nanoporous media.

In this work, the dynamics behaviors and equilibrium structures of self-assembly of surfactant molecules in supercritical CO<sub>2</sub> fluid, which were confined in slit-shape pores, have been studied by the classical molecular dynamics simulation. An amorphous structure is chosen as the solid surfaces of the slit-shape pores, in which the CO<sub>2</sub>-philic and CO<sub>2</sub>-phobic features have been designed, respectively, in order to analyze the various confined behaviors. The influence of the solid surfaces on the confined behaviors of surfactants in the Sc-CO<sub>2</sub> fluid phase has been investigated. Because a long simulation time is required for the amphiphilic self-assembly and adsorption on the surfaces, a simple coarse-grained model of the surfactant was adopted in this simulation, which includes the essential features of real surfactant molecules and ignores any irrelevant molecular details. The simulation results demonstrate that the quasirealistic surfactant model can capture the basic characteristics of the surfactant/Sc-CO<sub>2</sub> system and a more general trend can be extracted from the simulation. The rest of the paper is organized as follows. The simulation models and methods are provided in section II. The results and discussions are presented in section III, and finally, we conclude with a brief conclusion in section IV.

## **II. Methodology**

**Models.** In our simulation, the surfactant model was described as a linear  $H_4T_4$  structure, in which four CO<sub>2</sub>-philic units, identified as the "tail" group (T), show more affinity to the CO<sub>2</sub> solvent

<sup>(21)</sup> Fragneto, G.; Thomas, R. K.; Rennie, A. R.; Penfold, J. Langmuir 1996, 12, 6036. Eskilsson, K.; Yaminsky, V. V. Langmuir 1998, 14, 2444. Subramaniam,

V.; Ducker, W. A. Langmuir 2000, 16, 4447. Adler, J. A.; Singh, P. K.; Patist,

 <sup>(23)</sup> Lu, L. Y.; Berkowitz, M. L. J. Am. Chem. Soc. 2004, 126, 10254.
 (24) Senapati, S.; Berkowitz, M. L. J. Phys. Chem. B 2003, 107, 12906–

<sup>(24)</sup> Senapati, S., Berkowitz, M. L. J. Phys. Chem. B 2005, 107, 12900 12916.

<sup>(25)</sup> Senapati, S.; Keiper, J. S.; Desimone, J. M.; Wignall, G. D.; Melnichenko, Y. B.; Frielinghaus, H.; Berkowitz, M. L. Langmuir 2002, 18, 7371–7376.

 <sup>(21)</sup> Li, Zii, Jian, C. K. Langmar, 2004, 20, 6557–6566.
 (28) Shinto, H.; Tsuji, S.; Miyahara, M.; Higashitani, K. Langmuir 1999, 15, 578–586.

<sup>(29)</sup> Srinivas, G.; Nielsen, S. O.; Moore, P. B.; Klein, M. L. J. Am. Chem. Soc. 2006, 128, 848-853.

<sup>(30)</sup> Wijmans, C. M.; Linse, P. J. Phys. Chem. 1996, 100, 12583-12591.

<sup>(31)</sup> Bandyopadhyay, S.; Shelley, J. C.; Tarek, M.; Moore, P. B.; Klein, M. L. J. Phys. Chem. B **1998**, 102, 6318.

<sup>(32)</sup> Reimer, U.; Wahab, M.; Schiller, P.; Mogel, H. J. Langmuir 2001, 17, 8444.

#### Surfactant/Supercritical CO<sub>2</sub> Systems

than the other four CO<sub>2</sub>-phobic units, identified as the "head" group (H). This model surfactant could represent a number of prototypical nonionic surfactants. For example, in the previous molecular simulation studies, similar model surfactant was adopted to represent the real  $[F(CF_2)_n(CH_2CH_2O)_mH]^{33}$  or the [PVAc-b-PTAN]<sup>26,27</sup> surfactants in supercritical CO<sub>2</sub> fluid. The neighbor pairs of the units in the surfactant structure are bound together by a harmonic potential,  $U_{ij}$ , with spring length  $R_0$  and spring constant  $k^{b}$  (400 kcal/(mol Å<sup>2</sup>)) that is made sufficiently large so that the root-mean-square fluctuation in the bond length is about 2% of the equilibrium value ( $R_0 = 2.5$  Å)

$$U_{ij}(r_{ij}) = \frac{1}{2} k^b (r_{ij} - R_0)^2$$
(1)

where  $r_{ij}$  is the separation between particles *i* and *j*. We also consider the bond-angle bending potential by

$$U_{ij} = \frac{1}{2} k^{\theta} (\theta_{ijk} - \pi)^2$$
<sup>(2)</sup>

where  $k^{\theta} = 100 \text{ kcal/(mol rad}^2)$  is the bond bending force constant,  $\theta_{ijk}$  is the bond angle formed by the atoms *i*, *j*, and *k*, and  $\pi$  is the value of the equilibrium bond angle, which is chosen to be 180° in this simulation. Such an equilibrium bond angle may prevent surfactant chains from producing any sharp bends and increase an effective length of the surfactant.<sup>34</sup> The torsional potential was not included in this simulation mainly due to the use of enough large bond stretching and bending force constants with the 180° equilibrium bond angle in the CG model surfactant. A cut and shifted Lennard-Jones potential was used for the intermolecular and intramolecular (a pair of atoms three hops away in the surfactant chain) nonbonded interactions

$$U_{ij}(r_{ij}) = 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] - U_{ij}(r_{ij}^{\text{cut}}), \quad r_{ij} \le r_{ij}^{\text{cut}}$$
$$= 0 \quad r_{ij} > r_{ij}^{\text{cut}}$$
(3)

where  $\epsilon_{ij}$  and  $\sigma_{ij}$  are the well depth and the size parameters of the Lennard-Jones potential, respectively.

The parameters in the Lennard-Jones interactions were selected to mimic the qualitative phase behavior of surfactants in Sc-CO<sub>2</sub> fluid. The value of the size parameter for the tail group was chosen a little larger than that for the head group, which was based on the generally accepted fact that the CO<sub>2</sub>-philic tail group includes larger fluorinated segments. The size parameters of the head and tail sites in the model surfactant were chosen based on the reference reports.<sup>36</sup>

The determination of the set of interaction parameters (epsilon) for the surfactant was based on the consideration that the quasirealistic surfactant model can qualitatively reproduce experimental surfactant solubility dependence on Sc-CO<sub>2</sub> fluid density. In addition, the attractive interaction between the head groups (polar interaction) is made to be strongest, which is a primary driving force for micelle self-assembly. It is also a key factor for determining the solubility of the surfactants in the dense Sc-CO<sub>2</sub> fluid, since the intensity of the head-head attraction decides the extent to the penetration of the CO2 molecules to the head region.<sup>24</sup> In the surfactant/Sc-CO<sub>2</sub> systems,

Table 1. Interaction Parameters for the Surfactant/Sc-CO<sub>2</sub> Systems Investigated

type of		$\sigma_{ij}$	$\epsilon_{ij}$
interaction	$R_{ m CUT}/\sigma_{ij}$	(Å)	(kcal/mol)
CO <sub>2</sub> -CO <sub>2</sub>	2.5	3.72	0.469
CO <sub>2</sub> -head	2.5	3.56	0.650
CO <sub>2</sub> -tail	2.5	4.36	0.540
tail-tail	2.5	5.00	0.200
head-tail	2.5	4.20	0.290
head-head	2.5	3.40	0.935
CO <sub>2</sub> -philic wall-CO <sub>2</sub>	2.5	3.21	0.462
CO <sub>2</sub> -philic wall-head ( $\epsilon_{\rm H-W}$ )	2.5	3.05	0.100
CO <sub>2</sub> -philic wall-tail ( $\epsilon_{T-W}$ )	2.5	3.85	$0.500, 2.00^a$
CO <sub>2</sub> -phobic wall–CO <sub>2</sub>	$2^{1/6}$	3.21	0.462
CO <sub>2</sub> -phobic wall-head	2.5	3.05	$0.500, 2.00, 5.0^{b}$
CO <sub>2</sub> -phobic wall-tail	2.5	3.85	0.200

<sup>a</sup> Two different interaction energies between the CO<sub>2</sub>-philic wall and the tail group were considered in this study, in which the other interaction parameters keep unchanged. <sup>b</sup> Three different interaction energies between the CO<sub>2</sub>-phobic wall and the head group in this study.

the choice of parameters is to ensure that the interaction between the head group and the CO<sub>2</sub> solvent is stronger than that between the tail group and the solvent, since the polar block shows more attraction to CO<sub>2</sub> than the nonpolar block on account of the CO<sub>2</sub> quadrupole moment.27 The attractive interaction instead of completely repulsive interaction with a cutoff  $r_{ij}^{\text{cut}} = 2^{1/6}\sigma_{ij}$ , which is widely used in the previous simulations for model surfactants in aqueous systems, 35, 36-38 is employed in this surfactant model, in order to represent the actually existing interaction between the head and tail units in real surfactant molecules. This treatment including the attractive interaction of head-tail may produce a decrease in free surfactant monomers,<sup>35</sup> which instead form small-size aggregates or micelles even in lower concentration of surfactant. In light of the above criteria, we first adopted a set of reference parameter values and adjusted them by trial simulations. The reference LJ parameter values for the surfactant model can be obtained from the work of Hall et al.,<sup>27</sup> who studied the phase behavior of model surfactant/CO<sub>2</sub> systems using the discontinuous MD simulation. All of the nonbonded interaction parameters are listed in Table 1.

A single-point model<sup>39</sup> is used for the CO<sub>2</sub> molecule for the reason of computational economy. Sennapat25 et al. demonstrated that this simple model gives the same performance as the sophisticated EPM2 model<sup>40</sup> in the description of the pressure density dependence of supercritical CO<sub>2</sub> fluid. This simple CO<sub>2</sub> model has been successfully applied to simulate the reversed micelle behaviors of surfactant in supercritical CO<sub>2</sub> fluid.<sup>23,25</sup> Since a model surfactant with uncharged united groups was considered in this simulation, an uncharged single atom model for the CO<sub>2</sub> molecule is a consistent and reasonable choice.

The silica solid with an amorphous structure is chosen as the surface model. The classical well-established melt-quench procedure<sup>41-44</sup> was performed to generate the amorphous bulk silica structure. The detailed procedure has been described elsewhere.<sup>42</sup> Once the amorphous bulk silica was obtained, the

<sup>(33)</sup> Lisal, M.; Hall, C. K.; Gubbins, K. E.; Panagiotopoulos, A. Z. J. Chem. Phys. 2002, 116, 1171.

<sup>(34)</sup> Palmer, B. J.; Liu, J. Langmuir 1996, 12, 746-753.

<sup>(35)</sup> Talsania, S. K.; Rodriguez-Guadarrama, L. A.; Mohanty, K. K.; Rajagopalan, R. Langmuir 1998, 14, 2684-2692.

<sup>(36)</sup> Fodi, B.; Hentschke, R. Langmuir 2000, 16, 1626-1633.

<sup>(37)</sup> Simt, B.; Esselink, K.; Hilbers, P. A. J.; van Os, N. M.; Rupert, L. A. M.; Szleifer, I. Langmuir 1993, 9, 9-11.

<sup>(38)</sup> Karaborni, S.; Esselink, K.; Hilbers, P. A. J.; Smit, B.; Karthauser, J.; van Os, N. M.; Zana, R. Science 1994, 266, 254-256.

<sup>(39)</sup> Higashi, H.; Iwai, Y.; Uchida, H.; Arai, Y. J. Supercrit. Fuilds 1998, 13, 93-97

<sup>(40)</sup> Harris, J. G.; Yung, K. H. J. Phys. Chem. 1995, 99, 12021-12024.

<sup>(41)</sup> Litton, D. A.; Garofafalini, S. H. J. Appl. Phys. 2001, 89 6013.
(42) Rosenthal, A. B.; Garofalini, S. H. J. Am. Ceram. Soc. 1987, 70, 821.
(43) Yang, X. N.; Xu, Z. J.; Zhang, C. J. J. Colloid Interface Sci. 2006, 297, 38 - 44.

<sup>(44)</sup> Brodka, A.; Zedra, T. W. J. Chem. Phys. 1991, 95, 3710.

next step is to generate the silica surface. The two unrelaxed amorphous silica surfaces were obtained by fracturing the middle section of the bulk silica. Thereafter, a vacuum gap was inserted in the middle fracture section of the silica material. The gap separation is large enough (>50 Å) to eliminate any significant overlapping interactions between the bottom and top surfaces. The bulk structure was kept immobilized, and the fractural surfaces were relaxed first at 2000 K using MD simulations with 2ps NVT and 8ps NVE ensembles. Then, the system was cooled down stepwise to 300 K. This higher relaxation temperature will usually reduce the surface defect density. The surface defect concentration in the obtained silica surfaces is compatible with the features of the real silica glass surface.45 In this work, the main goal is to study the confined behaviors of surfactant in the pores with the silica-like surfaces, and thus, the detailed structure of the silica surface is not a major concern.

For the interaction between fluid molecules and the surface, only the oxygen atoms in the amorphous structure were considered. In order to investigate the influence of two kinds of amorphous silica surfaces, with obviously different affinity to the  $CO_2$  solvent, on the confined behavior of the surfactant/ $CO_2$ system, the CO<sub>2</sub>-philic and CO<sub>2</sub>-phobic surfaces were represented through adjusting the interaction between the surface and CO<sub>2</sub> molecule. We chose the cutoff radius to be 2.5  $\sigma_{ii}$  or  $2^{1/6}\sigma_{ii}$  for the CO<sub>2</sub>-philic and CO<sub>2</sub>-phobic surfaces, respectively.<sup>28</sup> The interaction energy parameters between the head/tail units of surfactants and the surfaces were also designed to be consistent with the interaction between the  $CO_2$  molecules and the surface. For the CO<sub>2</sub>-philic system, the stronger parameter is chosen for the interaction between the surfactant tails and surfaces as a result of the CO<sub>2</sub>-philic nature in the tail groups of surfactant. For the CO<sub>2</sub>-phobic surface, the interaction between the tail group and the surface is much weaker. Additionally, the pure repulsion interaction with the minimum cutoff is not used in order to reflect the actually existing interaction between the different groups of surfactant and surfaces. Finally, various values  $\epsilon_{T-W}$  and  $\epsilon_{H-W}$ energy parameters were evaluated in order to obtain reasonable surface adsorption for surfactant molecule through a series of trial simulations. The interaction parameters between the fluid molecules and the surface are also given in Table 1.

**Definition of Micelles.** To calculate the size of the aggregating micelle formed by surfactant monomers, we necessarily define a criterion based on a head—head distance to identify clusters unambiguously. If the separation between the two random head particles in different surfactant chains is less than the fixed contact distance (4 Å), which was justified by the head—head radial distribution function between the surfactants in the Sc–CO<sub>2</sub> fluid, the two surfactants are considered to be in the same cluster. The standard clustering procedure developed by Stoddard<sup>46</sup> was used to partition all of the surfactants into mutually exclusive clusters and to obtain the number of surfactants (*n*) in each aggregate.

**Simulation Details.** At first, the molecular dynamics simulations were carried out for the bulk surfactant/CO<sub>2</sub> phase in the isothermal–isobaric (NPT) and isothermal–isochoric (NVT) ensemble systems. The equations of motion were integrated using the velocity–Verlet algorithm with a time step of 2.0 fs. In the CG simulations, the time scales are usually 2 orders of magnitude larger than all atom simulation times, and it is common to use a larger time step due to smoother potentials brought by the CG model;<sup>29</sup> however, in view of the presence of the solid surfaces, the time step in this study is only 2 fs in order to avoid a possible large oscillation of the system stability. At the beginning of the simulation in this work, an energy minimization of the atomic coordinates of the system was performed in order to generate a reasonable starting point. The simulation systems contain 40–336 surfactant molecules, depending on various surfactant concentrations, and 16 384 solvent molecules. The NPT simulation for a period of 400 ps was first used to rapidly control the desired pressure of systems, corresponding to the supercritical condition. Both pressure and temperature were controlled using the Nose-Hoover algorithm with thermostat relaxation time of 1 ps in the simulations. Then, the NVT MD simulation run was done for a period of 1 ns, at which the energetic properties of the system are stabilized, and the system pressure oscillates around the desired pressure value. Finally, the production run over another period of 1 ns was performed in the bulk NVT simulation.

In all cases for the bulk-phase simulation presented above, the periodic boundary conditions were employed in all three directions. A typical demonstration of the simulation result for the system, with the surfactant mole fraction Xs = 0.00243, temperature T = 310 K, and the desired pressure P = 300 atm, is shown in Figure S1 of the Supporting Information, where the time evaluations of system pressure and energy are given. This result makes clear that the equilibration time for the bulk surfactant/Sc-CO<sub>2</sub> system is adequate. To validate the reasonability of the surfactant self-assembly in the bulk phase, we double the size of the simulation system as well as the simulation time. It has been found that there is no difference in the ASD, which is a good indication that the simulation procedure is rational.

In the following step, the MD simulations are carried out in the slit pores with amorphous silica surfaces, where the separation between the top and bottom surfaces obtained previously was adjusted to be an appropriate interval (114 Å), measured as the distance between the average heights in the top and bottom silica surfaces. The bulk surfacetant/Sc-CO<sub>2</sub> system obtained from the previous bulk-phase simulations was inserted into the slit pore. Throughout the MD simulations, the silica surface was held rigid to enhance the computational efficiency. The total systems, containing the 44 000-47 000 particles, were simulated in the NVT ensemble. The periodic boundary condition was applied in the two directions parallel to the surfaces. The individual simulation time is between 4 and 12 ns for each run with a total simulation time of 110 ns. This relatively long simulation time ensures to capture the complete dynamics and equilibrium behaviors of the confined surfactant/Sc-CO<sub>2</sub> system.

# **III. Results and Discussion**

First of all, we have to check whether the simple models for the CO2 and the model surfactant can represent the basic characteristics in the bulk surfactant/Sc-CO<sub>2</sub> solution. Figure S2 shows the percentages of surfactants  $(\eta)$  in small-size aggregates (n < 10) and those in big-size aggregates ( $n \ge 10$ ), at Xs = 0.0154 and T = 310 K, as a function of CO<sub>2</sub> pressure  $[P = 200 \text{ atm} (\rho = 0.67 \text{ g/cm}^3), 300 \text{ atm} (\rho = 0.83 \text{ g/cm}^3), \text{ and}$ 400 atm ( $\rho = 0.97$  g/cm<sup>3</sup>)]. There exists an increase in the surfactant percentage of small-size aggregates and a decrease of big-size aggregates with the CO<sub>2</sub> pressure increasing. This observation is consistent with the experimental behavior<sup>47</sup> that an increase in CO<sub>2</sub> density will enhance the surfactant solubility in supercritical CO<sub>2</sub>. At the same time, this obtained result (Figure S2) is also identical with the previous simulation reports,<sup>26</sup> where Scanu et al. first reproduced the experimental trends of the surfactant solubility with the Sc-CO<sub>2</sub> density using the lattice Monte Carlo simulation. This bulk-phase simulation manifests

<sup>(45)</sup> Du, J.; Cormack, A. N. J. Am. Ceram. Soc. 2005, 88, 2532.
(46) Stoddard, S. D. J. Comput. Phys. 1978, 27, 291.



**Figure 1.** Time evolution of the interaction energies of the surfactant-wall ( $U_{SW}$ ), surfactant-surfactant ( $U_{SS}$ ), and surfactant-CO<sub>2</sub> molecule ( $U_{SC}$ ) as well as the interface adsorption numbers (AN) of surfactants (a and b) at Xs = 0.00243 (left panel) and 0.0154 (right panel) for the weaker surface with  $\epsilon_{T-W} = 0.5$  kcal/mol.

that the model presented here is capable of representing the basic behaviors of the real surfactant/ $Sc-CO_2$  systems.

Confined Behaviors for CO<sub>2</sub>-Philic Surfaces. Dynamics Process. The dynamics process of the surfactant adsorption on the confined surfaces can be identified through the interactions between the system components that are responsible for the adsorption of surfactants. In this respect, the MD simulations of the adsorption dynamics process were performed with aggregated starting configurations, which were obtained by the bulk-phase simulations. Two CO<sub>2</sub>-philic surfaces with  $\epsilon_{T-W} = 0.5$  and 2.0 kcal/mol were considered, respectively. The simulation temperature is T = 310 K with various surfactant mole fractions (Xs = 0.00243, 0.00631, 0.0154, and 0.0201). The confined supercritical CO<sub>2</sub> fluid density is approximately 0.78 g/cm<sup>3</sup>. The time evolutions of the interaction energies of surfactantsurfactant ( $U_{SS}$ ), surfactant-CO<sub>2</sub> ( $U_{SC}$ ), and surfactant-surface  $(U_{SW})$  are demonstrated in Figure 1, at Xs = 0.00243 (left) and 0.0154 (right) on the CO<sub>2</sub>-philic surfaces with  $\epsilon_{T-W} = 0.5$  kcal/ mol.

In Figure 1, panels a and b, the interface adsorption numbers (AN) of surfactants, defined as the number of surfactants located within the range of 10 Å away from the two surfaces by identifying the tail group position, are also plotted for comparison. As shown in Figure 1, two distinctive processes are observed in the evolution of the three types of interaction energies during the simulation period. The fist step shows an obvious decrease in  $U_{SW}$  and  $U_{SS}$  and a slight increase in  $U_{SC}$ , corresponding to the adsorption dynamics process in the time intervals of 0 < t < 5.5 ns (left) and 0 < t < 7.5 ns (right) for the two different surfactant concentrations. The decreases in  $U_{SS}$  and  $U_{SW}$  are mainly owing

to two simultaneous combining processes of surfactant diffusion toward the surfaces and the surfactant reassembling, in which the surfactant molecules continuously reorganize to be in the closer packing form. Furthermore, an increase in the ANs of the surfactant with the time evolution confirms the surfactant diffusing process toward the surfaces.

However, the kinetics rate for the surfactant reassembly is obviously faster than that for the surfactant diffusion toward the surfaces. This can be clearly observed in Figure 1; that is, for lower surfactant concentration,  $U_{SS}$  can reach a reasonable fluctuation around mean values beyond a certain time of 3.7 ns, whereas  $U_{SW}$  becomes relatively stable at approximately 5.7 ns. A similar observation can be found for the higher concentration condition. This behavior suggests a slower process for the surfactant diffusion due to its lower mobility as compared with the surfactant reassembling, which usually needs a shorter time. At the same time, the rapid increase in  $U_{SC}$  is generally related to the rapid solvation process of surfactant within the confined space. Beyond a certain time point, 5.5 ns for Xs = 0.00234 and 7.5 ns for Xs = 0.0154, an equilibrium stage is attained for the two systems. During the equilibrium step, both the interaction energies ( $U_{SW}$ ,  $U_{SS}$ , and  $U_{SC}$ ) and the AN remain nearly unchanged with reasonable fluctuation, implying that the surfactant aggregate structures keep stable with no appreciable movement in the interfaces.

Figure 2 displays the typical snapshots of a representative aggregate at the various steps of the dynamics process for the system studied (Xs = 0.0154). In all of the snapshots, the CO<sub>2</sub> molecules are not shown for the sake of visual clarity. As seen in Figure 2, the surfactants form the aggregate in the rod-like



**Figure 2.** Snapshots of the stepwise evolution of absorption diffusion and structure reorganization (Xs = 0.0154) for a typical aggregate (containing 38 surfactants) on the CO<sub>2</sub>-philic surface with  $\epsilon_{T-W} = 0.5$  kcal/mol at the times of (a) 2.5, (b) 2.8, (c) 4, (d) 5.2, and (e) 9 ns, respectively. White spheres represent the tail particles and blue spheres head particles, and the amorphous surface atoms is shown by a reticular structure with yellow and red colors. The CO<sub>2</sub> molecules are not shown for visual clarity.

shape, which is identical with the observation by Fodi and Hentschke,<sup>36</sup> who used the same surfactant model (H4T4) in the simulation for an aqueous system. This aggregate in Figure 2, containing 38 surfactant molecules with the head locating in the core of the aggregate, initially situates in the region a little far from the solid surface and then slowly approaches to the surface mainly through the tail-surface interaction. It is evident to observe that the aggregate nearly keeps the stable structure in the moving process and finally lies on the surface in the shape of a rod with the tails standing on the solid, as shown in Figure 2e. It needs around 6.5 ns for this selected aggregate to complete the dynamics process. As expected, the higher surfactant concentration, at which larger-size aggregats are mainly formed, needs a longer time to achieve the required interface diffusion process. This can be demonstrated by comparing the two negative slopes of the adsorption  $U_{SW}$  curves: -1.13 for Xs = 0.00243 and -0.44 for  $X_s = 0.0154$  (cf. Figure 1). The slopes of  $U_{SW}$  curves represent the adsorption rate for surfactant molecules to approach the wall surfaces. The different adsorption rates between the two concentrations could be partly explained as, in lower surfactant concentration, the main formation of uimers and small-size aggregates, which possess higher mobility. Another possible factor is the available free wall surface area, which is gradually decreased with surfactant adsorption. With higher surfactant concentration, the adsorption rate becomes slower, which is also due to the obviously reduced free wall surface area. In the lower concentration condition, these relatively less and smaller surfactant aggregates or unimers in the fluid phase have a discontinuous and much faster adsorption process with higher frequency in adsorption and desorption, which makes more kinks in the AN and energy profiles, as shown in Figure 1a.

For the CO<sub>2</sub>-philic confined systems with higher interaction energy  $\epsilon_{T-W} = 2.0$  kcal/mol, Figure 3 shows the energy profiles of  $U_{SW}$ ,  $U_{SS}$ , and  $U_{SC}$  at Xs = 0.00243 (left) and 0.0154 (right). The whole dynamics process for the systems can also be represented by the nonequilibrium adsorption process, combining the interface diffusion and structure reorganization of surfactant molecules (<2.5 ns and <5.9 ns, respectively) and the equilibrium phase. During the first step in this case of Figure 3, the interaction energy  $U_{SW}$  and the ANs show a similar trend to the previous one with lower interaction surfaces. However, the time evolution of the interaction energy  $U_{SS}$  shows an increase, signifying a disruption of the large-size micelle structure and a possible formation of small aggregates. This is significant in contrast to those observed in Figure 1 and is attributed to the enhancement of the interaction between surfactants and surfaces. This behavior can be clearly observed in Figure 4, which displays that the stronger interaction surface leads to the structure deformation of the surfactant aggregate, when it comes near to the solid surfaces.

It is interesting to note that for the confined systems with stronger surface interaction, the equilibrium states for both the interface diffusion and the structure resembling processes of the surfactants have been achieved at nearly the same time. Furthermore, the slope of the  $U_{\rm SW}$  curve in Figure 3 is obviously higher than the corresponding one in the lower interaction surface (Figure 1) under the same surfactant concentration, which implies that the increased fluid—solid interaction increases the interface diffusion rate of surfactant aggregates. It should be noted that the above dynamics process is based on the specific initial configuration that is the so-called aggregated starting configuration. Different initial configurations may present different dynamics behaviors.

According to the above results, the surfactant concentration and the interaction strength have an obvious influence on the self-organization dynamics behaviors (including structure selfassembly and surface adsorption) of the surfactant/CO<sub>2</sub> on the solid/liquid interfaces. The enhancement in the adsorption energy usually leads to an increase of the absorbed amount of surfactant molecules and a disruption of the large-size micelle structure. Although this simulation is only conducted for this rod-like surfactant, we believe that the results extracted from this simulation are universally reasonable even for other types of surfactants (with various shapes of micelle).

210

160

110

10

40

8

60 NA



**Figure 3.** Same as Figure 1 except with  $\epsilon_{T-W} = 2.0$  kcal/mol.

Equilibrium Structure. In the following part, the equilibrium structures of the surfactant in the confined fluid-solid interfaces were evaluated, which is based on the equilibrium trajectory data. The density profiles of the tail groups and head groups of the surfactant ( $\rho_S$ , in mmol/cm<sup>3</sup>) and solvent ( $\rho_C$ , in g/cm<sup>3</sup>) between two types of surfaces are shown in Figure 5 for three various surfactant concentrations. The density profiles for the surfactants in the two opposite surfaces are not symmetrical because of the unlike structure for the two highly amorphous surfaces. For the two kinds of CO2-philic surfaces with different interaction strengths, pronounced solvent contact layers form near the surfaces. One can observe the density peaks of surfactant molecules near the surfaces. With the surfactant concentration increasing, the adsorption density peak becomes large. For the lower interaction surface (left panel), the adsorbed surfactant molecules are noticeably oriented, with the tail groups tethered to the surfaces and the head groups situated away from the surface. However, the orientation extent presented here on the amorphous surfaces is not as strong as that on the smooth hydrophilic potential pseudosurface,<sup>30</sup> where the heads of the absorbed surfactants uniformly cling to the smooth unstructured walls.

The density profiles of surfactant heads (left panel) in the interfacial region are relatively sharper and higher than those of tails, which is consistent with the more localized head units in the core of the micelles formed on the surfaces. Additionally, the tail density profiles display two peaks in the interfacial region, and the first peak closer to the wall is much bigger than the other one due to the surface interaction. The relatively higher peaks of the head density curves rightly locate between the two tail peaks in Figure 5. It seems to imply that the absorbed surfactants form an approximately bilayer aggregate structure on the CO<sub>2</sub>-philic surface with the head groups localized at the center of this structure. The aggregate shapes can be clearly shown in the snapshots of Figure 2. For the enhanced interaction surfaces (right panel in Figure 5), this orientation is not so obvious compared with the behavior for the weak interaction one, ascribed

to the fact that the surfactants adhere to the surface in a smaller separated distance. The results indicate that the adsorbed surfactants on the two surfaces are in different structures or morphologies (see Figure 4).

In order to further explore the influence of the initial configuration on the final simulated result, the density profiles of the tail groups and head groups of the surfactant and solvent with the random starting configurations between two types of surfaces are also shown in Figure S3 at  $X_S = 0.0154$ . The characters of the density profiles shown in Figure S3 are fairly consistent with those obtained from the aggregated starting configurations (shown in Figure 5). It indicates that different initial configurations have little influence on the final simulated results for our systems presented here.

The snapshots of the initial and final configurations of the confined fluid systems between the two CO<sub>2</sub>-philic surfaces at Xs = 0.0201 are shown in Figure 6. It is observed that surfactants in the initial configuration possess the self-assembling structure, which is located in the region away from the surfaces. At final equilibrium stages, the surfactant molecules form bilayer aggregate structures on the CO2-philic surfaces with energetically favorable contact between the tail groups and the surfaces, though this bilayer structure becomes unobvious on the stronger surface interaction case. The reorganized aggregates are formed on the weak interaction surface with the tail groups almost vertically pointing to the solid, as shown in the Figure 6a, whereas for the stronger interaction surface (Figure 6b), the surfactant molecules almost lie on the surfaces caused by the disruption of the aggregate structure. This observation further confirms the surface nature has a strong influence on the equilibrium topology of the adsorbed aggregates. We also present the final equilibrium snapshots for the random starting configuration in Figure S4, which are similar to those shown in Figure 6.

To quantify the adsorbed surfactant micelle sizes, the ASDs  $(\Phi(N))$  was evaluated for the confined systems with the two types of CO<sub>2</sub>-philic surfaces. Figure 7 shows the corresponding



**Figure 4.** Snapshots of the stepwise evolution of adsorption diffusion and structure reorganization for a typical aggregate (containing 22 surfactants) on the CO<sub>2</sub>-philic surface with  $\epsilon_{T-W} = 2.0$  kcal/mol at the times of (a) 3.1, (b) 3.2, (c) 3.5, and (d) 4 ns, respectively. The color scheme is the same as that in Figure 2. Left panel: side view; right panel: top view.

ASDs at Xs = 0.00243 (left panel) and 0.0154 (right panel), respectively. In the evaluation of the ASD, no distinction was made between adsorbed and nonadsorbed surfactants, since almost all surfactant molecules were adsorbed on the surfaces. As expected, a higher concentration produces large-size aggregates. Under a lower concentration (Figure 7, panels a and c), it is observed that, for the stronger interaction surface, the ASD exhibits only one big peak at a very small aggregate size value (N), representing almost unimers, whereas for the weak interaction surfaces, the distribution maximum of adsorbed surfactants is shifted to a higher value of N. However, under higher surfactant concentration, there are multipeaks in the ASD, which is similar to the observations by Shinto et al.28 and Palmer et al.34 using MD simulations. This multipeak behavior could be explained as the reason that the aggregates are partially breaking up and reforming during the course of MD simulation.34 Figure 7b indicates that, for the weak CO<sub>2</sub>-philic surface, the surfactant molecules were absorbed on the surface with the aggregate structure of relatively large sizes. However, for stronger adsorption interaction surfaces (Figure 7d), the proportion of monomers and small aggregates becomes larger in the adsorbed surfactants as a result

of enhanced interaction between the surface and the tail, which may destroy the micelle structures and enlarge the energetically favorable contact between the surfactants and the surfaces. The observation that the increased fluid—solid interaction can shift the peak position in the ASD curve and can change the structure of surfactants absorbed on the surface has also been observed by Wijmans et al.<sup>30</sup> using the lattice MC simulation.

The different interaction energies for the confined systems with the two CO<sub>2</sub>-philic surfaces have also been evaluated. Figure 8 gives the interaction energies of the surfactant-surface ( $U_{SW}$ ) and the surfactant-surfactant  $(U_{SS})$  with different surfactant concentrations. As expected, the interaction between surfactant molecules becomes large and the interaction between surfactant and surfaces reduces, as the concentration of surfactant increases. This is reasonable to consider the energetically preferable structure in larger aggregation formation, whereas the larger aggregate structure generally reduces the interaction between the surfactant and the surface. For the stronger interaction surface, the surfactant-surface interaction is scaled by 0.5 in Figure 8 for visual clarity. It is an absolutely predominant factor in the surfactant adsorption, especially for lower surfactant concentration, indicating a relatively complete contact between the surfactant molecules and the surface. This is realistic due to considerable surfactant molecules existing as either monomer or small aggregates on the surface. For the weaker interaction surface system, though most surfactants have been absorbed on the surface, the interaction between the surface and surfactant is very small as compared with the surfactant-surfactant interaction.

**Confined Behaviors for CO<sub>2</sub>-Phobic Surfaces.** For the confined system with CO<sub>2</sub>-phobic surfaces, a pure repulsive interaction between the surfaces and CO<sub>2</sub> molecules was chosen. A possible prototypical of the CO<sub>2</sub>-phobic plane is the silica surface with alkylation. The interaction between the tail and the surface is also weaker than the one between the head and the surface. At first, we studied the confined behaviors with  $\epsilon_{H-W} = 0.5$  kcal/mol. Compared to the CO<sub>2</sub>-philic surface, the dynamics process, mainly including the structure reorganization of surfactant, is relatively fast to reach a final equilibrium state. Details on the time evolution of various interactions on the confined system can be found in the Supporting Information (Figure S5). In the following section, the equilibrium structures of the surfactant/Sc-CO<sub>2</sub> in the confined pores with CO<sub>2</sub>-phobic surfaces have been investigated.

The density profiles for the tail and head groups of the surfactant molecules and the solvent molecules between the CO<sub>2</sub>-phobic surfaces are shown in Figure 9 for three various surfactant concentrations. Compared to the CO<sub>2</sub>-philic surface, the CO<sub>2</sub>-phobic surface repels the CO<sub>2</sub> solvent molecules and there is no solvent layer formation near the solid surfaces. It is interesting to note that there are also a few adsorption layers of surfactant molecules on the CO<sub>2</sub>-phobic surfaces and the surfactant molecules mainly show up in the central regions.

This surfactant depletion phenomenon on the surface is furthermore shown in the equilibrium snapshot of Figure 10 at Xs = 0.0154. This MD simulation also starts from the aggregate starting configuration, which is the same as the CO<sub>2</sub>-philic surface system. However, after equilibrium (even for 4 ns), the surfactant molecules within the slit pores show barely adsorption on the solid surface and most surfactants form aggregates in the region away from the surfaces. In order to test whether such a surfactantphobic interface behavior is just a coincidence, we have conducted two series of MD simulations: (I) with random starting configurations, which were generated by carrying out an equilibrated bulk MD simulation with no interaction between



**Figure 5.** Density profiles for the heads and tails of the surfactant molecules ( $\rho_s$ , in mmol/cm<sup>3</sup>) and for the CO<sub>2</sub> molecules ( $\rho_c$ , in g/cm<sup>3</sup>) on the CO<sub>2</sub>-philic surfaces with  $\epsilon_{T-W} = 0.5$  kcal/mol (left panel) and  $\epsilon_{T-W} = 2.0$  kcal/mol (right panel) at Xs = (a and b) 0.00243, (c and d) 0.00631, and (e and f) 0.0154.

the surfactants as described in ref 28; (II) with the surfactant micelles initially adsorbed on the solid surfaces, which was obtained from the previous CO<sub>2</sub>-philic systems. In all of the additional simulations, similar surfactant—phobic results were obtained, showing that the interfacial surfactant—phobic phenomenon in this simulation is indeed the characteristics for this confined surfactant/Sc-CO<sub>2</sub> system.

Hector et al.<sup>48</sup> performed the MD simulations for the surfactant/ water system on the TiO<sub>2</sub> and SiO<sub>2</sub> walls, which were considered to be hydrophilic and hydrophobic, respectively. In their simulation, the adsorption of the water molecules on the TiO<sub>2</sub> wall is obviously higher than on the SiO<sub>2</sub> wall, and the interface adsorption of the surfactant on the SiO<sub>2</sub> surface is very sparse.<sup>48</sup> Their simulation result was based on the bulk phase initially located at 5 Å from the surface and is consistent with the surfactant repulsion on the CO<sub>2</sub>-phobic surfaces in our study, where the initially located separation between the bulk phase and the surface is just 3 Å. This surfactant repulsion of the solid surface will be further discussed in the following section.

The equilibrium ASDs at Xs = 0.00243 and 0.0154 were shown in Figure 11 for the confined systems with the CO<sub>2</sub>phobic surfaces. For comparison, the ASDs in the bulk systems with the same fluid density and surfactant concentration are also plotted in Figure 11. Under lower concentration, the shape of the ASD for the bulk system shows that this bulk concentration (Xs = 0.00243) is below the CMC.<sup>49</sup> However, for the confined systems, under this lower concentration condition, the surfactant molecules mainly form small aggregates. Figure 11b shows the ASDs for both the confined systems and the bulk phase at Xs = 0.0154, which should be far higher than the bulk-phase CMC based on the curve trend. As compared with the bulk system, the surfactant micelles in the confined system (Xs = 0.0154) possess relatively larger aggregate sizes.

For the CO<sub>2</sub>-phobic systems, the percentage of small aggregate (PSA) as a function of the overall surfactant concentration is shown in Figure 12, together with the related result in the bulk phase. The proportion of small aggregate becomes decreased with the concentration increasing. For the higher surfactant concentration, the effect of solid surfaces on the percentage of the small micelles becomes minor. This is because at the higher concentration condition surfactant molecules mainly form larger micelle structures. It appears that the bulk system produces more small-size aggregates in comparison with the confined systems. This behavior is consistent with the results in Figure 11. The CMC can also be quantified according to the results of Figure 12. There are several methods of determining the CMC.<sup>49,50</sup> In this research, we defined the CMC as the surfactant concentration in which the number of surfactant molecules participating in the small-size micelles (n < 5) is equal to that in the large-size aggregates. This method has been adopted by Wijmans and Linse,<sup>50</sup> and it has been proved to be relatively reasonable. In Figure 12, The CMC was marked by the intersection point between the fitted curve through the simulation results and the straight line parallel to the abscissa through the position of PSA = 0.5.

<sup>(48)</sup> Dominguez, H.; Goicochea, A. G.; Mendoza, N.; Alejandre, J. J. Colloid Interface Sci. 2006, 297, 370–373.

<sup>(49)</sup> Panagiotopoulos, A. Z.; Floriano, M. A.; Kumar, S. K. *Langmuir* **2002**, *18*, 2940–2948.



Figure 6. Snapshots of the initial and final confined fluid configurations between the two  $CO_2$ -philic walls at Xs = 0.0201. White and blue spheres represent the tail and head units of the surfactants. The green color is used to represent the  $CO_2$  solvent.



**Figure 7.** Aggregate size distribution (ASD,  $\Phi(N)$ ) at Xs = 0.00243 (left panel: (a) and (c)), and 0.0154 (right panel: (b) and (d)), The top panel and bottom panel are for the weaker and stronger interaction surfaces, respectively.

The CMC of the surfactant solution confined within the  $CO_2$ phobic surfaces is clearly lower than that of the bulk system. It appears that the  $CO_2$ -phobic solid surface has a certain effect on the CMC of the surfactant solution. This behavior could possibly be related to the influence of pore wall confinement, which might increase the collision possibility among surfactant molecules.

Figure 13 gives the various interaction energies for the CO<sub>2</sub>phobic confined systems. Similarly, the interactions between surfactants ( $U_{SS}$ ) increase with the surfactant concentration. As compared with the bulk system, the confined systems demonstrate stronger interactions between surfactant molecules. This is realistic in consideration of larger size aggregates formation and less monomer existence in the confined pores. The reduction of the interaction between surfactant and CO<sub>2</sub> indicates that the surfactant solvation in the Sc-CO<sub>2</sub> solvent decreases with the surfactant concentration increasing. It appears that the presence



**Figure 8.** Equilibrium interaction energies between surfactants ( $U_{SS}$ ) and between the surfactant and wall ( $U_{SW}$ ) vs the total surfactant concentration (Xs), for the two different CO<sub>2</sub>-philic surfaces. For the strong interaction surface, the surfactant-surface interaction energy is divided by 2 for visual clarity.



**Figure 9.** Density profiles of the heads and tails of the surfactant  $(\rho_s, \text{ in mmol/cm}^3)$  and for the CO<sub>2</sub> molecules density distributions  $(\rho_c, \text{ in g/cm}^3)$  on the CO<sub>2</sub>-phobic surfaces with  $\epsilon_{\text{H-W}} = 0.5$  kcal/mol at Xs = (a) 0.00243, (b) 0.00631, and (c) 0.0154.

of the solid surface enhances the interaction between surfactant molecules and reduces the interaction between the  $CO_2$  and surfactant molecules.

For the CO<sub>2</sub>-phobic surface, the MD simulations were also carried out with the further enhanced interaction parameter, such as  $\epsilon_{H-W} = 2.0$  kcal/mol and  $\epsilon_{H-W} = 5$  kcal/mol (10 times the previous one). It is observed that there are still hardly surfactant molecules adsorbed on the CO<sub>2</sub>-phobic surfaces for both cases, as shown in Figure S6 of the Supporting Information. In the



**Figure 10.** Snapshot of final equilibrium configuration on the CO2phobic surface with  $\epsilon_{H-W} = 0.5$  kcal/mol at Xs = 0.0154. White and blue spheres represent the tail and head units of the surfactants. The green color is used to represent the CO<sub>2</sub> solvent.



**Figure 11.** Aggregate size distribution ( $\Phi(N)$ ) at Xs = (a) 0.00243, and (b) 0.0154, for the confined systems within CO<sub>2</sub>-phobic surfaces and the bulk-phase systems without the surfaces.

confined systems, the force balance of the interaction between solvent and surface, the interaction between solvent and surfactant, and the interaction between the surfactant and surface decides the distribution of surfactants in the confined space.<sup>48</sup> This surfactant-phobic behavior in the confined systems with the CO<sub>2</sub>-phobic surfaces implies that there is a stronger barrier near the surfaces, which impedes the movement of the surfactant molecule toward the surfaces. In the previous simulation studies,<sup>51,52</sup> when the solute approaches the solid surfaces, the free-energy barrier of solute transfer is correlated with the solvent density, that is, the largest free energy barrier coinciding with the region of the lowest solvent density. Thus, in the CO<sub>2</sub>-phobic systems, the significant depletion of CO<sub>2</sub> solvent density near the surfaces

<sup>(51)</sup> Kerisit, S.; Parker, S. C. Chem. Comm. 2004, 52-53.

<sup>(52)</sup> Kerisit, S.; Parker, S. C. J. Am. Chem. Soc. 2004, 126, 10152-10161.



**Figure 12.** Mol percentages of surfactants forming the small-size aggregates (PSA) vs the total surfactant concentration (Xs) for the confined systems within the  $CO_2$ -phobic surfaces and the bulk-phase systems. Arrows indicate the critical micelle concentrations (CMC).



**Figure 13.** Interaction energies between surfactants ( $U_{SS}$ ) and between the surfactant and CO<sub>2</sub> molecule ( $U_{SC}$ ) vs the total surfactant concentration (Xs) for the confined systems within the CO<sub>2</sub>-phobic surfaces and the bulk-phase systems.

may lead to a strong energy barrier for surfactant adsorption. This has been verified by the additional MD simulations, in which the same interaction parameters as the CO<sub>2</sub>-phobic system in Table 1 have been applied except for using the larger interaction cutoff ( $\sigma_{cutoff} = 2.5\sigma_{C-W}$ ) between CO<sub>2</sub> and the surfaces. According to the simulation results, for different initial configurations, the adsorption of surfactants on the surface can be clearly observed. The additional simulations give possible evidence that the surface adsorption of CO<sub>2</sub> solvent plays an important role in determining the interface behaviors of surfactants on solid surfaces. Another cause is the absence of long-range forces (e.g., electrostatic) in the model system, which may produce different attractive interactions between surfactants and surfaces. Further research using an atomic-model simulation is necessary to explore this concern.

#### **IV.** Conclusion

In this study, we have performed coarse-grained molecular dynamics simulations to study the dynamics and equilibrium behaviors of surfactant/Sc–CO<sub>2</sub> mixtures confined in the slit pores with amorphous structure surfaces. The surfactant model consists of two building blocks representing the CO<sub>2</sub>-philic units

and the  $CO_2$ -phobic units, respectively. The  $CO_2$ -philic and  $CO_2$ phobic surfaces were introduced by truncating the interaction potential at various cutoff separations between the  $CO_2$  molecules and the surfaces. This model system could effectively probe and describe the microscopic phenomena such as adsorption and self-organization of the surfactants on such surfaces with reasonable length and time scales.

Adsorption dynamic processes for the surfactant/CO<sub>2</sub> system on the CO<sub>2</sub>-philic surfaces with two various fluid-solid interaction energies between the surfactant tails and the surfaces were presented by evaluating the various energy profiles. For the weaker interaction surface, the surfactant molecules continuously reassemble to be in close proximity and the aggregate structure continues to be a steady rod-like morphology during the interface diffusion process. However, for the stronger interaction surface, the aggregates possess a tendency of structure dissociating once they approach the surface, which is not identical to the observation for the weaker interaction surface. The enhancement in the adsorption energy usually leads to an increase of the absorbed amount of surfactant molecules.

The equilibrium structures of the surfactant in the fluid-solid interfaces were analyzed on the basis of the equilibrium configuration data. For the two  $CO_2$ -philic surfaces with different interaction strengths, the density profiles and the aggregate size distributions of the surfactant molecules in the absorption layer show a different morphology and structure. Evaluation of the configuration snapshots indicates that the surfactants absorbed on the stronger interaction surfaces are mainly in the form of monomer and small aggregates, but for the weaker interaction surface, the surfactant aggregates show larger-size structures. It has also been demonstrated that different initial configurations have little influence on the final equilibrium structures for adsorbed surfactant molecules.

For the CO<sub>2</sub>-phobic surfaces, there are hardly surfactants adsorbed on the surfaces, even though we greatly reinforce the interaction strength between the surfactant heads and the surfaces. It is possibly attributed to the presence of solvent diminution near the solid—liquid interface, which may produce a free-energy barrier near the surfaces and hinder the adsorption of surfactant. The CMC of the surfactant solution confined within the CO<sub>2</sub>phobic pores is clearly lower than that of the corresponding bulk system. This behavior could be influenced by the pore wall confinement.

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**Supporting Information Available:** (1) The time evaluations of system pressure and energy in the bulk-phase simulation with the surfactant concentration  $X_S = 0.00243$ , temperature T = 310 K, and pressure P = 300 atm. (2) The percentages of surfactants in small-size aggregates and those in big-size aggregates as a function of CO<sub>2</sub> pressure. (3) The density profiles and final equilibrium snapshots for the random starting configuration. (4) Details on the time evolution of various interaction energies on the CO<sub>2</sub>-phobic confined surfaces with  $\epsilon_{H-W} = 0.5$  kcal/mol. (4) Simulated results for the CO<sub>2</sub>-phobic surface with  $\epsilon_{H-W} = 2.0$  kcal/mol and  $\epsilon_{H-W} = 5$  kcal/mol. This material is available free of charge via the Internet at http://pubs.acs.org.

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