Modeling Gas–Liquid Interfaces by Dissipative Particle Dynamics: Adsorption and Surface Tension of Cetyl Trimethyl Ammonium Bromide at the Air–Water Interface

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ABSTRACT: Adsorption of surfactants at gas–liquid interfaces that causes reduction in the surface tension is a classical problem in colloid and interface science with multiple practical applications in oil and gas recovery, separations, cosmetics, personal care, and biomedicine. Here, we develop an original coarse-grained model of the liquid–gas interface within the conventional dissipative particle dynamics (DPD) framework with the goal of quantitatively predicting the surface tension in the presence of surfactants. As a practical case-study example, we explore the adsorption of the cationic surfactant cetyl trimethyl ammonium bromide (CTAB) on the air–water interface. The gas phase is modeled as a DPD fluid composed of fictitious hard-core “gas” beads with exponentially decaying repulsive potentials to prevent penetration of the liquid phase components. A rigorous parametrization scheme is proposed based on matching the bulk and interfacial properties of water and octane taken as the reference compounds. Quantitative agreement between the simulated and experimental surface tension of CTAB solutions is found for a wide range of bulk surfactant concentrations (∼10⁻⁹ to ∼1 mmol/L) with the reduction of the surface tension from ∼72 mN/m (pure water) to the limiting value of ∼37.5 mN/m at the critical micelle concentration. The gas phase DPD model with the proposed parametrization scheme can be extended and applied to modeling various gas–liquid interfaces with surfactant and lipid monolayers, such as bubble suspensions, foams, froths, etc.

1. INTRODUCTION

Multiple industrial, personal care, and biomedical applications of surfactants, such as detergent action, oil recovery, flotation, and drug delivery, are based on their ability to affect the interfacial phenomena at the boundaries between immiscible phases. Composed of hydrophilic head and hydrophobic tail fragments, amphiphilic surfactants are preferentially adsorbed at the interfaces and aggregate in bulk liquid phases forming micelles and mesophases. Surfactant adsorption controls the surface tension and facilitates formation of stable bubble dispersions and emulsions. Experimental measurement of the surface tension as a function of the surfactant composition is a tedious process. With the advancement of computational tools and resources, there is an increasing demand for efficient methods for calculations of the surface tension of various colloidal systems. While the simulation methods of liquid–liquid interfaces are well developed, modeling of gas–liquid interfaces remains challenging. Here, we develop a novel dissipative particle dynamics (DPD) model of the liquid–gas interface with the goal of qualitatively predicting the surface tension in the presence of surfactants.

As a practical case-study example, we explore adsorption of the cationic surfactant, cetyl trimethyl ammonium bromide (CTAB), on the air–water interface. CTAB is a quaternary ammonium surfactant, widely used in industrial and biomedical applications. There are a number of experimental studies of CTAB aqueous solutions, in which the surface tension, γ, is measured as a function of the bulk surfactant concentration, c_bulk. The collection of this data is presented in Figure 1a. Despite a substantial degree of uncertainty among the published data, the general trend, that is typical of most surfactant systems, is clearly seen. At low concentrations, surfactant molecules adsorb and form a monolayer at the air–water interface. As the surfactant concentration increases, γ reduces monotonically from the pure water surface tension of 72 mN/m to the limiting value of γ_CMC = 37.5 ± 1 mN/m that corresponds to the onset of micelle formation in the bulk solution occurring at the critical micelle concentration (CMC), c_{CMC} ≈ 0.9 ± 0.1 mmol/L. Beyond CMC, the experimentally measured surface tension remains unchanged.

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The classical Gibbs thermodynamics provides a solid foundation for interpretation of experimental data on the surface tension and the surface concentration of surfactants. The Gibbs equation links the surface concentration $\Gamma$ at the given bulk surfactant concentration, $c_{\text{bulk}}$, and temperature $T$, with the surface tension isotherm, $\gamma(c_{\text{bulk}})$, as

$$\Gamma(c_{\text{bulk}}) = -\frac{1}{nRT} \frac{d\gamma}{d\ln c_{\text{bulk}}}$$

where $R$ is the gas constant and $n$ is the dissociation number: $n = 1$ for a nonionic surfactant, and it equals the number of ions in a dissociated ionic surfactant, which in the case of CTAB is equal to 2 (see Section SI, Supporting Information). 18–20 The Gibbs equation (eq 1) assumes that the bulk surfactant solution is ideal, which is a reasonable approximation, as the bulk surfactant concentration is sufficiently small below CMC. Equation 1 can be used for estimating the surfactant surface concentration from experimental data on the surface tension without invoking any particular model for the surfactant adsorption. Applicability of eq 1 for cationic surfactants, such as CTAB, has been intensively discussed.12,13

The monolayer adsorption of surfactants is generally described in terms of the Langmuir adsorption isotherm$^{19,21}$

$$\Gamma = \Gamma_0 \frac{K_L c_{\text{bulk}}}{1 + K_L c_{\text{bulk}}}$$

where $\Gamma_0$ is the maximum surface concentration of surfactants or the monolayer capacity, and $K_L$ is the reduced Henry constant. It is worth noting that the monolayer capacity $\Gamma_0$ should not be mistaken for the limiting surface concentration $\Gamma_{\text{CMC}}$ at the CMC. Although these values are often considered to be the same, the ideal monolayer of maximum capacity is not achievable in experiments because of the surfactant aggregation in the bulk, above the CMC. Note that eq 1 is applicable for interpreting experimental data only below CMC (as the surface tension is unchanged beyond CMC, see Figure 1a), while eq 2 can be extended up to the theoretical maximum capacity $\Gamma_0$.

Integration of the Gibbs equation (eq 1) assuming the Langmuir adsorption isotherm (eq 2) leads to the relationship between the surface tension, $\gamma$, and the surfactant bulk concentration, $c_{\text{bulk}}$, known as the Szyszkowski equation$^{12}$

$$\gamma = \gamma_0 - nRT \ln(1 + K_L c_{\text{bulk}})$$

where $\gamma_0$ is the surface tension of pure water at $c_{\text{bulk}} = 0$. For the reasons stated above, the Szyszkowski equation is applied only to pre-micellar dilute solutions ($c_{\text{bulk}} < \text{CMC}$). Experimental data for CTAB taken from six different sources$^{12−17}$ are fitted to the Szyszkowski equation with the monolayer capacity $\Gamma_0 = 4.37 \times 10^{-7}$ mmol/cm$^2$ and reduced Henry constant $K_L = 4481$ cm$^2$/mmol. This correlation shown in Figure 1a provides excellent agreement with experimental data over 3 decades, for $c_{\text{bulk}} < \text{CMC}$. The surface tension at an experimental CMC value of $c_{\text{CMC}} \approx 0.9 \pm 0.1$ mmol/L in the Szyszkowski fit perfectly agrees with the reported values of $\gamma_{\text{CMC}} = 37.5 \pm 1$ mN/m. With the values of $\Gamma_0$ and $K_L$ determined from the Szyszkowski fitting, one can find the relationship between the surface and bulk concentrations, or the adsorption isotherm, $\Gamma(c_{\text{bulk}})$, using the Langmuir equation (eq 2), see Figure 1b. This relationship gives the surface concentration of $\Gamma_{\text{CMC}} = (3.5 \pm 0.05) \times 10^{-7}$ mmol/cm$^2$ at $c_{\text{CMC}} \approx 0.9 \pm 0.1$ mmol/L, which is in agreement with the values reported in the literature; for example, Adamczyk et al.13 and Okuda et al.12 found, respectively, $\Gamma_{\text{CMC}} = 3.45 \times 10^{-7}$ and $3.085 \times 10^{-7}$ mmol/cm$^2$. It is worth noting that the experimental surface concentration at CMC is smaller than the theoretical monolayer capacity.

Using the Langmuir isotherm (eq 2), the Szyszkowski equation (eq 3) is further converted into the relationship between the surface tension of the surfactant monolayer and the surfactant surface concentration, which results in the Frumkin equation$^{22,23}$

$$\gamma = \gamma_0 - nRT \Gamma_0 \ln\left(1 + \frac{\Gamma}{\Gamma_0 - \Gamma}\right)$$

The respective correlation for the CTAB experimental data with $\Gamma_0 = 4.37 \times 10^{-7}$ mmol/cm$^2$ is plotted in Figure 1c. This equation is useful for the analysis of the theoretical and simulation models of surfactant monolayers, which predict the interfacial tension as a function of the surface concentration. Thermodynamic equations (eqs 1–4) are used below to verify the consistency of the DPD model and demonstrate the agreement between the simulated and experimental data.

Using the parameters $\Gamma_0$ and $K_L$ determined from the fit of the experimental data on the surface tension (Figure 1a) to
Szyszkowski eq 3, the sought relationship between the surface and bulk concentrations can be constructed assuming the Langmuir adsorption eq 2. This relationship in the form of Langmuir equation is shown in Figure 1b. It is worth noting that the surface concentration can be directly assessed by the neutron reflection.24 The neutron reflection data on CTAB surface adsorption32 measured at a higher temperature (303 K) is qualitatively similar to the data presented in Figure 1, see Section SV, Supporting Information. It should be noted that despite excellent agreement with experimental data in Figure 1a, the conventional Langmuir model (eq 2) does not take into account the electric double layer (EDL) effects at the interface and the contributions to the surface adsorption from the counterions present in the diffused layer, which are considered in more advanced models.30–28

Molecular mechanisms and specifics of surfactant adsorption have been explicitly demonstrated on many systems with atomistic molecular dynamic (MD) simulations.29–34 In particular, Tomassone et al.35 performed MD simulations of Lennard-Jones particles to study the adsorption isotherm of nonionic surfactants at the gas–liquid interface and calculated the surface tension as a function of the surfactant concentration without a detailed comparison to experimental data. Klein and co-workers studied a series of linear alkyl benzene sulfonates36 and found that the monolayer surface tensions and the surfactant orientations depend on the chain length and degree of branching of the surfactants, while Zhao et al.37 investigated the effects of inorganic salts on the formation of alkyl benzene sulfonate monolayers and observed that the presence of counterions might decrease the thickness of the air–water interface. Several studies investigated the properties of lung surfactant monolayers38–46 consisting of different phospholipids, such as dipalmitoyl phosphatidyl choline (DPPC), cholesterol, and surfactant proteins, focusing on the pressure–area isotherms and surfactant two-dimensional (2D) phases such as liquid-expanded (LE) and liquid-condensed (LC) phases. Most interesting to this study are the studies on modeling CTAB monolayers. Yuan et al.47 analyzed structural properties of CTAB monolayers at two different surface concentrations, using MD simulations, estimating the monolayer thicknesses. Yazhgur et al.48 performed MD simulations of CTAB monolayers with the added electrolyte at air–water interfaces and found that the interaction between adsorbed CTAB molecules changes from repulsive to attractive as the surface concentration increases. However, few attempts were made to model adsorption and surface tension of practical surfactants when the results could be compared with experimental data. It is noteworthy that even the calculations of pure water surface tension require quite sophisticated methods to get an agreement with the experiment.49 In their recent work, Rios-López et al.50 modified the standard interatomic force field for CTAB–water interactions to bring the surface tension, calculated using TIP4P/ε or SPCE water models, closer to experimental data.

In general, atomistic simulations provide important qualitative information on the phase behavior and structure of surfactant monolayers, quantitative predictions of adsorption isotherms and surface tension are hindered by small lengths and timescales. For these goals, coarse-grained (CG) models come forefront, and in the first place, CGMD with the MARTINI force field.51 The CG MARTINI52,53 model has been applied to study mechanical properties, the phase behavior of lung surfactant monolayers, and the interfacial adsorption.54–57 Wang et al.58 performed MARTINI CGMD simulations to study the specifics of the stability of sodium dodecyl sulfate (SDS) foam films against entering of oil droplets and subsequent emulsification. Anogiannakis et al.59 predicted key properties of the self-assembly of surfactants (SDS, CTAB, dodecyltrimethylammonium bromide (DTAB), and octyltrimethylammonium bromide (OTAB)) such as the critical micelle concentration (CMC) and micellar size, with a semi-quantitative agreement with the experimental results. However, applications of the MARTINI force field for modeling surfactant monolayers at the air–water interface generally lead only to semi-quantitative results, as this force field underestimates the air–water surface tension to a considerably low value of 30 mN/m. Illa-Tuset et al.60 compared atomistic and MARTINI results of the CTAB self-assembly into micelle formation in water and the interfacial behavior of monolayers at water–vacuum and water–organic solvent interfaces, and showed that MARTINI reproduced atomistic results only semi-quantitatively.

The SPICA61 force field deserves special attention. It was specifically developed to model interfacial systems by CGMD. SPICA, which is an extended version of the Shinoda–DeVane–Klein (SDK) force field62 was initially developed for nonionic surfactants and liquids and later extended to zwitterionic63 and ionic surfactant64 systems and membranes containing cholesterol.65 Parametrization of SDK and SPICA force fields is based on matching the interfacial properties of the system under consideration, such as the surface tension and area per surfactant, and consequently, these models reproduced the experimental pressure–area isotherms for DPPC monolayers,63 micellar size66 of SDS, among other systems. However, this parametrization scheme involves laborious calculations of free energies, and the transferability of the model is afflicted due to specificities required to match experimental quantities.

As a practical alternative to CGMD, DPD has been widely used to investigate various interfacial processes, including micelle formation of surfactants,67,68 phase separation in immiscible binary liquid mixtures,67 and droplets on surfaces in shear flow.68 However, the standard DPD framework69–71 was designed to model liquid–liquid systems and the soft-core DPD potentials cannot simulate the sharp variation of the fluid density at the gas–liquid interface. The DPD fluid equation of state is quadratic in density that prohibits the gas–liquid coexistence. To remedy this limitation of standard DPD, the multi-body DPD (MDPD) method72,73 was developed, in which interaction parameters depend on the local density of the beads. Ghoufi and Malfreyt performing MDPD simulations, calculated the surface tension 74,75 and developed an efficient MDPD parametrization approach for surfactant systems at the air–water interface,76 the transferable parameters of which reproduced the experimental water surface tension value of 71 mN/m and an increase of the surface tension upon addition of the salt. Goujon et al.77 observed small oscillatory effects in the dependence of surface tension on the surface area at liquid–vapor and liquid–liquid interfaces in different CG models, MARTINI, DPD, and MDPD. Wu et al.78 investigated the sliding dynamics of nano bubbles on surfaces using MDPD, who showed that the bubble motion is influenced by the surface wettability and roughness. Yong et al.79 studied nanoparticle-mediated evaporation at liquid–vapor interfaces and observed that the evaporation rate decreases as the wettability of the nanoparticles reduced. The
This model dihard-core DPD particles with exponential repulsive potentials. The proposed model is based on the standard DPD imentally observed surface tension and surfactant adsorption the density variation across the gas
cores exponential potential is in providing the ability to mimic colloidal suspensions, prevents the penetration of liquid beads

In an attempt to improve MDPD simulations of gas

surfaces using MDPD simulation to study the e
eff of the surfactant surface tension with

MDPD method is also used to model the surface adsorption of surfactants at the gas-water interface. Recently, Chu et al. investigated surfactant adsorption of dodecyldimethylamine oxide (DDAO) at the gas-water interface and observed that surface adsorption continued to increase even after CMC is reached. The equilibrium surface tension of DDAO monolayers was found to be 70 mN/m, which is higher than the experimental data ~33 mN/m and the authors attributed this to the high surface-to-volume ratio in simulations compared to macroscopic systems. Zhou et al. modeled the adsorption of the ionic surfactant (DTAB and SDS) on smooth and rough surfaces using MDPD simulation to study the effect of surfactant adsorption on the resistance of wall-bound flows. In an attempt to improve MDPD simulations of gas microbubbles, Pan et al. combined MDPD and standard DPD models by introducing the gas phase standard DPD beads at low density while modeling the liquid phase by MDPD. However, using the MDPD method did not give a good agreement of the surfactant surface tension with experimental data. Alternatively to MDPD, Tran-Duc et al. analyzed the rheology of dilute bubble suspensions using the standard DPD framework, in which the gas bubble was modeled as an individual particle interacting with liquid beads with a hard-core exponential repulsive potential. This potential, which was introduced earlier by Pan et al. for modeling colloidal suspensions, prevents the penetration of liquid beads into the bubble. The advantage of the introduction of the hard-core exponential potential is in providing the ability to mimic the density variation across the gas-liquid interface. In this work, we develop a DPD model for simulating gas-liquid interfacial phenomena, which reproduces the experimentally observed surface tension and surfactant adsorption isotherm. The proposed model is based on the standard DPD framework and represents the gas phase as built of fictitious hard-core DPD particles with exponential repulsive potentials. This model differs from the combined DPD-MDPD approach of Pan et al. as the standard DPD parametrization is used modeling the liquid phase and the interactions between the solvent (water) and surfactant. Our model is simpler and more feasible compared to MDPD. It is, in some respects, similar to the free volume approaches in the self-consistent field theory (SCFT) to model surfactant monolayers at the air-water interface. The key of the proposed model is a rigorous parametrization scheme that is based on reproducing the

experimental surface tension and atomistically simulated interfacial density profiles of reference systems (water and octane). The model details, parametrization, and computational setup are discussed in Section 2. In Section 3, we demonstrate the consistency of the gas phase model parametrization and present the results of the simulations of CTAB adsorption on the water-air interface and surface tension calculations. Special attention is paid to the comparison of the calculated results with the experimental and atomistic MD simulation data. Conclusions are summarized in Section 4.

2. DISSIPATIVE PARTICLE DYNAMICS MODELING

2.1. DPD Formalism. In the standard DPD framework, the simulated systems comprised coarse-grained (CG) soft-core beads interacting via pairwise forces. DPD beads obey Newton’s laws of motion

\[
dr_i \frac{dv_i}{dt} = f_i = \sum_{j \neq i} (F_{ij}^C + F_{ij}^B + F_{ij}^E + F_{ij}^T + F_{ij}^F)\]

where \( r_i, v_i, \) and \( m_i \) are, respectively, the position, velocity, and mass of the \( i \)th particle. The total force \( f_i \) on the particle \( i \) due to the interactions with other particles is the sum of the pairwise conservative \( (F_{ij}^C) \), bond \( (F_{ij}^B) \), electrostatic \( (F_{ij}^E) \), dissipative \( (F_{ij}^D) \), and random \( (F_{ij}^F) \) forces. The conservative force is short-ranged, it has a simple repulsive soft-core linear form, \( F_{ij}^C(r_{ij}) = a_i \left( 1 - \frac{r_{ij}}{R_c} \right)^2 \) where \( a_i \) is the conservative repulsion parameter, \( R_c = |r_i| = |r_j| \), the radial distance between \( i \) and \( j \) particles, and \( r_{ij} = |r_i - r_j| \). \( R_c \) is the interaction cutoff beyond which \( F_{ij}^C \) vanishes, and for this reason, it can be considered as the effective bead diameter.

Bond forces are taken to be arising from either the harmonic potential, \( V^B(r_{ij}) = k_b (r_{ij} - r_{ij}^0)^2 \), where \( r_{ij}^0 \) is the equilibrium separation between the bonded beads \( i \) and \( j \). The finite extensible nonlinear elastic (FENE) type, \( V^E_{ij} = -k_E r_{max}^2 \ln \left[ 1 - \left( \frac{r_{ij}}{r_{max}} \right)^2 \right] \) with \( r_{ij} \) the equilibrium bond length, and \( r_{max} \) the maximum deviation of the bond length from \( r_{ij} \).
The long-ranged electrostatic interactions are modeled with the smeared charge approach\textsuperscript{8,90} in which point charges are replaced by charge distributions. Following González-Melchor et al.\textsuperscript{88} we employ the Slater-type, exponentially decaying charge distributions, \( \rho_Q(r) = \frac{Q}{\sigma Q} \exp \left( -\frac{r}{\lambda} \right) \). Then, the electrostatic force between two beads of charges \( Q_i \) and \( Q_j \) is given by

\[
F_{ij}^{\text{el}}(r_{ij}) = \frac{e^2}{4\pi} \frac{Q_i Q_j}{r_{ij}^3} \left( 1 - \frac{r_{ij}}{\lambda} \right) \frac{1 + \frac{r_{ij}}{\lambda}}{1 + \frac{r_{ij}}{\lambda}},
\]

where \( \Gamma = e^2/(\kappa_B T \epsilon_0 \epsilon_r R_0) \), defined by Groot\textsuperscript{89} \( \epsilon_0 \) and \( \epsilon_r \) are, respectively, the permittivity of free space and dielectric constant of water. \( \lambda \) is the smearing parameter, determining the spread of the charge distribution, which is tuned to match the correct electrostatic force between the two charges. The dissipative and random forces, which constitute the Langevin thermostat, are also short-ranged with the cutoff \( R_{c} \) and are given by \( F_{ij}^{\text{fr}}(r_{ij}) = -\gamma D(r_{ij})(v_{ij} - v_{ij}) \) where \( v_{ij} = v_i - v_j \) the relative velocity between the pair of particles \( i \) and \( j \), \( \gamma D \) is the friction coefficient, \( \sigma = \sqrt{2k_B T R_c} \), and \( \theta_{ij} \) is a Gaussian random variable. The weight functions, \( w^D \) and \( w^R \), are correlated and chosen to obey the fluctuation–dissipation theorem.\textsuperscript{90}

2.2. Parametrization of Liquid Phase Interactions. The CTAB–water system DPD parameters are chosen from our previous work\textsuperscript{84} with the coarse-graining scheme with the beads consisting of \( N_{m} = 4 \) heavy atoms (Figure 2a). The water \( W \) bead represents four water molecules and has the effective diameter \( R_{c} = 0.711 \) nm. The CTAB surfactant ion (CTA\textsuperscript{+}) is represented by a linear chain consisting of one positively charged head \( H \) bead and four tail \( T \) beads. The counter bromide ions of the surfactant are modeled as hydrated bromide anions (\( A^- \)) and are taken to be the same bead type as water beads but carrying a negative charge, representing the bromide ion and three water molecules. The size of all beads equals the size of the \( W \)-bead. A coarse-graining scheme is depicted in Figure 2a. The standard DPD intracomponent conservative parameter between the same bead types, \( a_{ii} = 106.5 k_B T/R_{c0} \) is found by matching the water compressibility at a coarse-graining level \( N_{m} = 4 \). The intercomponent parameters are found by matching the infinite dilution activity coefficients (IDAC),\textsuperscript{92} the tail \( T \) beads interact with water beads with a mismatch parameter \( \Delta a_{TW} = a_{TW} - a_{ii} = 23.4 k_B T/R_{c0} \) while the \( W \)-\( W \) interaction is favorable with \( \Delta a_{WW} = 0 \) and the tail–head interaction is only moderately repulsive (\( \Delta a_{TH} = 5 k_B T/R_{c0} \)). In our earlier work,\textsuperscript{93} FENE type 1–2 bonds among \( T \) and \( H \) beads are found to be superior in reproducing atomistic radial distributions, and therefore the 1–2 bonds in CTA\textsuperscript{+} are represented by FENE bond types. In addition to 1–2 bonds \( (T \sim T, T \sim H) \), 1–3 bonds \( (T \sim (T \sim T), T \sim (T \sim H)) \) are used to account for the chain stiffness, which are represented by harmonic bonds. The electrostatic smearing parameter in eq 7 is chosen to be \( \lambda = 0.25 R_{c} \) while the Groot’s constant is \( \Gamma = 1.067 \) for \( N_{m} = 4 \). The long-range contribution to the electrostatic energy is estimated with the Ewald sum, using a \( k \)-vector set of 10. All conservative and bond parameters are displayed in Table 1. For a detailed description of the CTAB–water parametrization see ref 91.

### Table 1. DPD Conservative Repulsion \( a_{ij} \) and Bond Parameters\textsuperscript{a}

<table>
<thead>
<tr>
<th>conservative repulsion parameters ( a_{ij} (k_B T/R_{c0}) )</th>
<th>bond type</th>
<th>( k_{ij} (k_B T/R_{c0}) )</th>
<th>( r_0 (R_{c0}) )</th>
<th>( r_m (R_{c0}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( W ) \rightarrow ( T ) (hydrophilic head ( H ) &amp; tail ( T ) beads)</td>
<td>FENE</td>
<td>280</td>
<td>0.605</td>
<td>2.0</td>
</tr>
<tr>
<td>( T ) \rightarrow ( T ) (hydrophobic beads)</td>
<td>harmonic</td>
<td>300</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>( T ) \rightarrow ( H ) (head ( H ) &amp; tail ( T ) beads)</td>
<td>harmonic</td>
<td>150</td>
<td>1.3</td>
<td></td>
</tr>
</tbody>
</table>

\( ^{a} \) Parameters \( a_{ij} \) and \( b_{ij} \) for \( j \neq G \) correspond to the G-bead hard-core interaction force (eq 8).

2.3. DPD Gas Model. We introduce a model of the gas phase consisting of fictitious DPD \( G \)-beads securing the gas density. \( G \)-beads have the same size and number density as other beads and the \( G \)–\( G \) intracomponent interaction is described by the same soft-core linear repulsive force \( (a_{GG} = a_{ij}) \) as other system beads, but are “lighter” with a smaller mass of 0.015 to keep the relative mass density in correspondence to the water beads.\textsuperscript{84} \( G \)-beads prevent penetration of the liquid phase components into the gas phase via an exponentially decaying hard-core repulsive pairwise force instead of the conservative soft-core linearly decaying force, \( F_{ij}^{G}(r_{ij}) \). The repulsive force between gas \( G \)-beads and liquid \( j \)-beads has the following form

\[
F_{ij}^{G} = \begin{cases} 
    a_{Gj} \left( 1 - \frac{e^{e_{Gj}/R_{c0}}}{1 - e^{e_{Gj}/R_{c0}}} \right) \hat{r}_{ij}, & \text{if } r_{ij} < R_{c0} \\
    0, & \text{if } r_{ij} \geq R_{c0}
\end{cases}
\]

This force increases steeply as the particles start overlapping (as shown in Figure 2b), making the \( G \)-beads effectively hard-core compared to the conventional DPD soft-core beads. \( a_{Gj} \) and \( b_{ij} \) are the parameters controlling the strength and steepness of the force. The hard-core exponential force (eq 8) was introduced by Pan et al.\textsuperscript{84} for modeling colloidal suspensions and was used for modeling microbubbles.\textsuperscript{84} We determine the parameters, \( a_{Gj} \) and \( b_{ij} \) by matching with the experimental surface tension and atomistically simulated interfacial density profiles of pure water and octane chosen as the references, as described in Section 3.1. This parametrization is the key to the proposed model: it provides transferability of the interaction potentials for different surfactants represented by the chains of hydrophilic (head) and hydrophobic (tail) beads. The gas interaction parameters of the bromide ion and the head group beads \( H \) are taken to be the same as that of water beads, which is reasonable as the bromide ion is hydrated and \( H \) is strongly hydrophilic. In the cases when the head groups are of varying hydrophilicity (such as in poly(ethylene oxide) (PEO)), they can be parameterized with suitable reference compounds (such as ethylene/propylene oxide groups) that are used for the standard DPD.
parametrization. The values of \( a_{Gj} \) and \( b_{Gj} \) parameters are shown in Table 1.

2.4. System Setup and Simulation Details. Simulations of the CTAB—air—water system are performed in a \( 30 \times 30 \times 50 \) \( R_c^3 \) box, with 135,000 total beads and the number density \( \rho = 3/R_c^{3.1,10} \). The commonly used value for friction coefficient is \( \gamma_0 = 4.5 \), while the time step \( \delta t \) is set to 0.001 \( \tau \), an order of magnitude smaller than the usual DPD time step due to the steep potential between the liquid and gas beads. The initial system configurations are constructed by sandwiching the equilibrated water slab between two gas slabs with the initial configuration of an equal number of surfactant molecules \( N_0 \) placed at each interface: CTA’ cations are placed at the interface in a regular quadratic fashion in normal orientation and the bromide anions \( Br^- \) are randomly distributed in the water phase, Figure 2c. Several simulations are performed by varying the initial number of surfactants \( N_c \) at each of the two interfaces, from 0 to 1200 (see Section SIII, Supporting information), and the surface tension is estimated using the Irving and Kirkwood (IK) method\(^{2,6,9}\).

\[
\gamma_{\text{sim}} = \frac{1}{2} \int_{-L_z/2}^{L_z/2} [p_Z(z) - p_L(z)] \, dz
\]

(9)

where \( p_Z(z) \) is the pressure normal to the interface and is equal to \( p_L(z) \), the pressure tensor component in the \( Z \) direction, whereas the lateral pressure is given by \( p_L(z) = \frac{1}{2}[p_{xx}(z) + p_{yy}(z)] \). The factor 1/2 in eq 9 accounts for the fact that our setup has two interfaces (Figure 2c). The surface tension obtained from the simulations is converted to real units using \( \gamma = \gamma_{\text{sim}} \times k_BT/R_c^2 \), with \( R_c = 0.711 \) nm and \( T = 298 \) K.

Simulations are performed in the NVT ensemble, with \( R_c \) and \( k_BT \), respectively, being the units of length and energy/temperature. The velocity Verlet algorithm is employed to solve the equations of motion (eqs 5 and 6).\(^{7,11} \) All simulations are run for 4 million steps with at least 1 million steps used for averaging, costing about 3200 CPU hours for each. We employ the DL_MESO package\(^{7,12} \) for all our DPD simulations, which we modified to incorporate the hard-core DPD interaction (eq 8) for the gas particles. Snapshots of the systems are created by VMD software.

3. RESULTS AND DISCUSSION

3.1. DPD Gas Model Interaction Parameters. We propose a rigorous strategy for parametrization of the hard-core exponential repulsion force (eq 8) between gas and liquid phase beads, which provides the parameter’s transferability between different surfactants within the same coarse-graining scheme that represents the surfactant molecules as the chains of hydrophilic (head) and hydrophobic (tail) beads of the same size. We chose pure water and octane as reference liquids and determine the parameters, \( a_{Gj} \) and \( b_{Gj} \) by matching with the experimental surface tension and atomistically simulated interfacial density profiles of water—air and octane—air interfaces. Octane is taken as a reference for parametrization of tail T beads and is modeled as composed of dimers of T beads (the single T bead compound would represent butane, which is not a liquid under ambient conditions).\(^{32} \) The interaction parameters between the liquid phase beads are taken from previous simulations of micellization in bulk surfactant solutions,\(^{91} \) as described in Section 2.2. For parametrization of G—W and G—T interactions, we simulate the systems with 50% liquid (water composed of W-beads and octane composed of T—T dimers) and 50% gas composed of G-beads (as in Figure 2c, but without surfactants) with the gas—liquid interactions modeled with the hard-core force (eq 8). Parameters \( a_{Gj} \) and \( b_{Gj} \) (\( j \) states for W- or T-beads, respectively, for water—air and octane—air systems) are varied independently and the surface tension is calculated for each \( (a_{Gj}, b_{Gj}) \) pair. The set of \( (a_{Gj}, b_{Gj}) \) pairs that reproduce the experimental air—liquid surface tension for water (72 mN/m) and octane (21.1 mN/m) within a certain accuracy (±3 mN/m for water and ±2.4 mN/m for octane) is determined. These sets of \( (a_{GW}, b_{GW}) \) and \( (a_{GT}, b_{GT}) \) pairs are presented in Figure 3a. In fact, an increase of both parameters, the repulsive strength, \( a_{Gj} \), and the steepness, \( b_{Gj} \), leads to an increase of the interbead repulsion, and respectively, an increase of the surface tension.

Figure 3. (a) Sets of \( (a_{Gj}, b_{Gj}) \) pairs corresponding to the surface tension \( 72 \pm 3 \) mN/m in the gas—water system (solid black line) and the surface tension \( 21.1 \pm 2.4 \) mN/m in the gas—octane system. (b) DPD calculated water density profile across the air—water interface for different pairs of \( (a_{GW}, b_{W}) \) parameters along with the density profile from the atomistic simulation\(^{47} \) (black). (c) DPD and MD density profiles across the interface in octane—gas system.
interfaces. The DPD computed and reference atomistic MD density profiles are given in Figure 3b,c. For water, we present published MD results that simulated with the standard SPC/E water model at the box of lateral length scales of 24 nm. For octane, we present our original data obtained using the COMPASS-II force field (see the details in Section SIV, Supporting Information). In both cases, a good agreement between DPD and MD simulations is found for the steepness parameters \( b_{Wj} > 15 \). The increase of \( b_{Wj} \) values induces a sharper variation of the repulsive force that requires smaller time steps to be used in the simulations. So, we choose \( b_{GW} = 20 \) and the corresponding pair value of \( a_{WG} = 32.6 \, k_B T / R_c \) as the parameters of the hard-core exponential repulsive force between G- and W-beads that gives the surface tension of 71.83 ± 3.6 mN/m in DPD simulations. For octane, we have chosen the same value of \( b_{GT} = 20 \) with the pair value of \( a_{GT} = 25.3 \, k_B T / R_c \) that corresponds to the simulated surface tension of 22.91 ± 2.1 mN/m, close to the experimental value. These pairs of parameters are used in DPD simulations to model repulsion of hydrophilic (W, H, and A) and hydrophobic (T) beads of liquid phase components with gas G-beads, see Table 1.

3.2. CTAB Adsorption at the Air–Water Interface. Using the gas phase model developed and parameterized against pure water and octane systems, we consider adsorption of CTAB on the water–air interface. Simulations of CTAB surfactant monolayers at the air–water interface are started from the initial configuration of an equal number of surfactant molecules \( N_0 \) placed at each interface: CTA⁺ cations are placed at the interface in a regular fashion and the bromide anions \( \text{Br}^- \) are randomly distributed in the liquid phase, Figure 2c. The system is equilibrated, the surface concentration surfactant \( \Gamma_s \) is counted, and the surface tension \( \gamma \) is calculated using eq 9. By increasing the total number of surfactant molecules and the respective surfactant concentration up to the CMC, the sought dependence of the surface tension as a function of the surface concentration is determined; the obtained dependence is shown below in Figure 6c.

Upon system equilibration from the initial configuration, most of the \( \text{Br}^- \) anions quickly diffuse to the interface and associate with CTA⁺ cations forming the Stern double layer; some anions (very few) remain in the solution forming a diffuse layer. CTA⁺ cations rearrange and stay at the interface. Only upon the approach of the CMC, some CTA⁺ cations diffuse into the solution, associate with \( \text{Br}^- \) anions, and form micelles (see Table S1, Supporting Information). The surface concentration is calculated as \( \Gamma_s = N_s / (N_A A) \), where \( N_s \) is the average equilibrium number of CTA⁺ cations at the water–air interface. \( A \) is the total area of the interface (\( A = 30 \times 30 \, R_c^2 \)) and \( N_A \) is Avogadro’s number. The respective area per molecule is given as \( A_s = 10^{15} / (N_A \, \Gamma) \, \text{Å}^2 \). At surfactant concentrations \( c_s < \text{CMC} \), we find very few cations in the

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**Figure 4.** Snapshots of the equilibrated CTAB in the gas–water system at different surface concentrations: (a) \( N_0 = 300 \), (b) \( N_0 = 900 \), and (c) \( N_0 = 1200 \). Colors: T-green, H-yellow, A-purple, water-blue, and gas-pink.

**Figure 5.** (a–c) Partial density distributions of all bead types in different gas–water–CTAB systems: (a) \( N_0 = 300 \), (b) \( N_0 = 900 \), and (c) \( N_0 = 1200 \). The insets provide a closer look at PDDs of T, H, and A beads. (d) Average distances of T–H and A–H peaks as a function of the surface concentration.
solution, \( \sigma \sim \sigma_0 \) as practically all cations remain at the water–air interface. The statistics is not sufficient to calculate the equilibrium bulk concentration due to the limited size of the simulation box. Figure 4 shows typical snapshots of the equilibrated systems. At low surfactant concentrations (\( \Gamma_0 = 300 \); \( \Gamma_s = 1.1 \times 10^{-7} \) mmol/cm\(^2\), \( A_s = 152 \) Å\(^2\)/molecule), surfactant molecules are well isolated at the interface and oriented parallel to the interface (Figure 4a). At a higher surface concentration (\( \Gamma_0 = 900 \); \( \Gamma_s = 3.3 \times 10^{-7} \) mmol/cm\(^2\), \( A_s = 51 \) Å\(^2\)/molecule), the monolayer becomes denser, the surfactant molecules start interacting with each other forcing the surfactant tails to orient in the normal direction (Figure 4b). In this case, some of the CTA\(^+\) cations are pushed into the water phase, indicating that the monolayer approaches the maximum surface concentration \( \Gamma_0 \). The orientation transition is gradual with the tail–interfacial angle increasing with the surface concentration \( \Gamma_s \); observed monolayer structures are similar to those in MD simulations.\(^{29,48}\) A further increase in the surfactant concentration leads to formation of micelles in the water phase, as shown in Figure 4c, at \( \Gamma_0 = 1200 \); \( \Gamma_s = 3.95 \times 10^{-7} \) mmol/cm\(^2\) and \( A_s = 42 \) Å\(^2\)/molecule. Due to a small size of the simulation box, the micelle formation is suppressed, however, the qualitative behavior observed in experiments (see below in Figure 6a) and the onset of this micellization corresponding to the CMC is well reproduced.

From the snapshots in Figure 4, the 2D symmetry (in the X, Y directions) of the distribution of different beads at the interface and the bulk phases can be inferred while quantitative information can be obtained from the partial density distributions (PDD) along the normal z direction. The PDDs of different components in the systems, water and air phases, surfactant tails and heads, and the counter anions, are depicted in Figure 4a–c, in the three cases corresponding to Figure 4a–c. At the surfactant concentration below CMC (Figure 5a,b), all surfactant ions and a majority of counterions reside at the interface, while a small amount of counterions reside in the bulk. This picture is consistent with the classical models of ionic surfactant adsorption, where surfactants and counterions form an electric double layer (EDL) or Stern layer at the interface while a small portion of counterions exist in the diffuse layer in the bulk. For ionic surfactants, effects due to electrostatic interactions arise from the counterion/co-ion adsorption at the EDL described by Gouy, Chapman, and Stern,\(^{100}\) and the influence of diffusing ions in the diffuse layer beyond the EDL needs to be accounted in the Gibbs adsorption equation (eq 1).\(^{26}\) There have been several theoretical approaches that attempted to model the EDL and the diffuse layer effects,\(^{101–105}\) however, in a case where the ionic concentration in the diffuse layer is negligible, one may assume equal surfactant and counterion adsorption at the interface and neglect the diffuse layer effects.\(^{14}\) Figure 5a,b shows that the distributions of the H\(^+\) ions and A\(^-\) ions nearly overlap and peak closer (see insets), and thus the amount of counter anions appearing in the bulk water phase is negligible. Furthermore, the near-peaked H and A distributions also indicate that the counter anions intercalate between the surfactant (CTA\(^+\)) cations, which supports the common approximation that adsorption of surfactant ions and counterions in the Stern layer at the interface are nearly equal and the contribution to the surface tension from the diffuse layer is negligible.\(^{14}\)

The density distributions in Figure 5c shows micellization by the presence of surfactant cations and anions in the middle of the bulk water phase. From the distributions in Figure 5a–c, it is also clear that the tail orientation changes from parallel to normal to the interface with an increase in the surfactant concentration, as the width of the tail distributions changes from very narrow in Figure 5a to wider in Figure 5c. The average T–H peak-to-peak distance \( t_{\text{AH}} \) is an increasing function of the surfactant surface concentration \( \Gamma_s \) (Figure 5d), until the onset of micellization, beyond which it levels off since the surfactant monolayer gets saturated. On the other hand, the A–H peak-to-peak distance \( t_{\text{AH}} \) remains constant over the entire range of surfactant concentrations (Figure 5d), as \( t_{\text{AH}} \) is determined by the electrostatic interaction between the oppositely charged CTA\(^+\) and Br\(^-\) ions, which is strong and not much influenced by the neighboring ions.

### 3.3. Comparison with the Experimental and Atomistic Simulation Data

Comparison of the simulation and experimental data is not straightforward. While in the simulations, we determine the dependence of the surface tension on the surface concentration, \( \gamma_{\text{sim}}(\Gamma) \), in the experiments the surface tension is measured as a function of the bulk concentration of the surfactant, \( \gamma_{\text{exp}}(c_{\text{bulk}}) \), as shown in Figure 6a. Neither in simulations nor in experiments, the adsorption isotherm, i.e., a relationship between the surface and bulk concentrations, \( \Gamma(c_{\text{bulk}}) \), is directly determined. As noted above, this situation is remedied by the general thermodynamic relations based on the Gibbs adsorption equation (eq 1),

![Figure 6](https://dx.doi.org/10.1021/acs.langmuir.0c02572 Langmuir 2020, 36, 14686–14698)
which allow us to establish the theoretical correlations between the bulk concentration, surface concentration, and surface tension. Assuming that the monolayer adsorption is described by Langmuir equation (eq 2), the experimental data, \( \gamma_{\exp}(c_{\text{bulk}}) \), can be fitted by the Szyszkowski equation (eq 3). This fit that perfectly approximates the CTAB experimental data from six different literature sources (Figure 6a) allows us to estimate the monolayer capacity \( \Gamma_0 \) and reduced Henry constant \( K_0 \) and predict the adsorption isotherm by the respective Langmuir equation (eq 2), Figure 6b. Further, the Langmuir isotherm (Figure 6b), that relates surface and bulk concentrations, \( \Gamma(c_{\text{bulk}}) \), can be used to correlate the simulated surface tension with the bulk surfactant concentration, as \( \gamma_{\text{sim}}(c_{\text{bulk}}) \). This correlation is shown in Figure 6a.

Taking into account the inherent limitations of the coarse-grained models and finite-size effects due to periodic boundary conditions in the simulation box, the obtained correlation of the simulated and experimental data over the range of surfactant concentrations spanning 3 decades shown in Figure 6 is excellent. Our model perfectly predicts the gradual reduction of the surface tension from the pure water value of 72 mN/m at a low surfactant concentration up to about 30% of the monolayer capacity, somewhat underestimates experimental data at moderate adsorption (30–60% of the monolayer capacity), and, what is worth noting, perfectly fits the extension of the Frumkin equation beyond the experimental CMC, reasonably reproducing the limiting value of \( \gamma_{\text{CMC}} = 37.5 \pm 1 \text{ mN/m} \) measured in the experiments at and above CMC.

The system behavior at CMC deserves special attention. Experimental CMC is achieved at \( c_{\text{CMC}} \approx 0.9 \pm 0.1 \text{ mmol/L} \). Beyond CMC, the surface concentration and, respectively, the surface tension, do not change much as seen in Figure 6a. We performed a special simulation of the bulk CTAB solution using a larger simulation box (40 × 40 × 40 \( R^3 \)) with an increasing surfactant concentration (see Section SII, Supporting Information). The onset of micellization was found at \( c_{\text{CMC,sim}} \approx 1.9 \text{ mmol/L} \), in agreement with the earlier work that used the same parametrization of the CTAB-water system. In the simulations of the CTAB–air–water systems, micelle formation is clearly observed at the surface concentrations >3.9 × 10^{-7} \text{ mmol/cm}^2 (see Section SIII, Supporting Information). The surface concentration at the onset of micellization can be estimated to be \( \Gamma_{\text{CMC,sim}} \approx (3.8–3.9) \times 10^{-7} \text{ mmol/cm}^2 \) that agrees with the estimate of the CMC in bulk simulations (red region in Figure 6b). The surface tension above \( \Gamma_{\text{CMC,sim}} \) in DPD simulations is found to be 26–29 mN/m (red region in Figure 6c), which is lower than the experimental value 37.5 ± 1 mN/m (Figure 6a), yet well agrees with the extension of the Frumkin equation beyond the experimentally measured range. This observation, as well as the overestimation of the CMC in the bulk simulations can be attributed to the finite-size effects. Overestimation of CMC calculated from bulk simulations can also result from the fitting procedure used. The high surface-area-to-volume ratio of the simulation box and limited timescales of simulation runs hinder micelle formation and stabilize highly compressed monolayers. An additional factor that may contribute to the delay of micellization in simulations is related to the initial configuration of dense monolayers at the interfaces, which may remain in a metastable state beyond the CMC.

Another way of presentation of the surface concentration and tension of surfactant monolayers employs the notions of the area per surfactant molecule in the units of \( A^2 \), \( A = 10^{10}/(N \Gamma) \), where \( \Gamma \) is in \text{mol/cm}^2, and the surface pressure is defined as the difference between the surface tensions of the pure solvent and the monolayer, \( \Pi = \gamma_0 − \gamma \). This approach is frequently used for presenting experimental data as well as the results of the simulations. The equilibrium area per surfactant \( A_{\text{CMC}} \) of CTAB at \( \Gamma_{\text{CMC}} \) was calculated by several groups, the value of which deviates substantially among these authors. Manna and Panda calculated \( A_{\text{CMC}} \) to be 34 \( A^2 \)/molecule, and Rodriguez et al. reported 39 \( A^2 \)/molecule, while our DPD results gives 42 \( A^2 \). In comparison, \( A_{\text{CMC}} \) obtained from the averaged experimental data in Figure 6a using the Frumkin equation is around 47 \( A^2 \)/molecule at \( \Gamma_{\text{CMC}} \) and 38 \( A^2 \)/molecule in the theoretical limit of the monolayer capacity \( \Gamma_0 = 4.37 \times 10^{-7} \text{ mmol/cm}^2 \).

Figure 7 illustrates the surface tension and pressure dependencies of the molecular area obtained in our DPD simulations in comparison with experimental data and the recent atomistic MD simulations of Rios-López et al. The authors modified the standard force field for CTAB to improve the match with experimental data and performed MD simulations for two water models, SPC/E and TIP4P. To the best of our knowledge, this work provides the closest correlation with experimental data published so far in the literature, despite the apparent underestimation of the surface tension.

Figure 7. (a) Surface tension and (b) surface pressure of the CTAB monolayers at the gas–water interface, as a function of the area per surfactant molecule at the interface.
tension and, respectively, overestimation of the surface pressure. Our DPD results demonstrate a much better agreement with experimental data in the whole range of surfactant concentrations. Note that the deviations from MD results are more prominent for the surface tension (Figure 7a), since the MD underestimated the surface pressure of pure water: \( \gamma_{0,\text{MD}} = 69 \text{ mN/m} \) compared to the experimental and DPD values of \( \sim 72 \text{ mN/m} \). For the surface pressure dependence (Figure 7b) this difference is canceled, and the MD results are somewhat closer to the DPD data.

4. CONCLUSIONS

We suggest an original coarse-grained DPD model for studying gas–liquid interfaces and predicting surfactant adsorption and surface tension. The model developed is verified and tested against experimental data on the CTAB ionic surfactant monolayers on the water–air interface. The quantitative agreement with experimental data on the surface tension of CTAB solutions is found within 3 orders of surfactant concentrations (\( \sim 10^{-3}–1 \text{ mmol/L} \)) starting from the surface tension of pure water (\( \sim 72 \text{ mN/m} \)) down to the minimum value of \( \sim 37.5 \text{ mN/m} \) achieved at the CMC (\( \sim 0.9 \text{ mmol/L} \)). This agreement with experimental data from six independent sources\(^{12–17} \) is unmatched in the literature. The simulations performed at varying surfactant concentrations reveal the mechanisms of the monolayer formation beyond the onset of micellization at the CMC. We confirm the applicability of the general thermodynamic equations of Gibbs, Langmuir, Szyszkowski, and Frumkin for interpretation of the simulation data and correlation with experiments. We found from the simulation results that the concentration dependence of the surface tension fit the theoretical predictions extended beyond the experimental CMC. The proposed model is based on a rigorous parametrization scheme that can be transferable for other liquid–gas systems with various surfactants and/or lipids.

We use the conventional DPD framework,\(^{71} \) which represents the system compounds as built of beads composed of several atoms or molecules with the equal bead size and intracomponent soft-core repulsive parameters. Following our earlier work on modeling CTAB–water solutions,\(^{91} \) the coarse-grained scheme is based on water W-beads comprising four water molecules and surfactant (tail and head) beads comprising four heavy atoms of the effective diameter \( R_e = 0.711 \text{ nm} \). The electrostatic interactions are accounted for within the smeared charge approximation. The proposed model represents the gas phase as a DPD fluid composed of fictitious hard-core DPD beads of the same size and density as the liquid phase beads. To prevent penetration into the gas phase, the beads of the liquid phase species (water and surfactant) are repelled from the gas beads by exponentially decaying hard-core force.

The rigorous parametrization scheme is based on matching the experimental and atomistically simulated properties of the reference compounds such as, water, octane, and other compounds.\(^{92} \) The matching properties for parametrization of water–surfactant (liquid phase) interactions include the water density and compressibility, water–octane solubility quantified by infinite dilution activity coefficients, and radial distribution functions along the alkane oligomer chains. The parameters of water–CTAB interactions are taken from ref 85. The water–air and octane–air surface tension, and water and octane density profiles across the liquid–air interface are used for parametrization of the repulsive exponential hard-core forces between the gas beads and hydrophilic (water) and hydrophobic (tail) beads.

The proposed gas phase model implemented with the conventional DPD framework has apparent advantages compared to the coarse-grained MD and many body DPD methods suggested in the literature for simulating gas–liquid interfaces and surfactant monolayers. The method is more computationally efficient and provides the quantitative agreement with experimental data on the surfactant adsorption isotherm, concentration dependence of the surface tension, and CMC. The parameters determined for the CTAB–water solution with a proper adjustment according to the employed parametrization scheme can be used for other surfactant and lipid systems. Further studies are needed to demonstrate the applicability of the proposed approach for modeling other surfactants by varying the alkyl chain length, addition of salt, or by changing the headgroup from cationic to anionic. Also it should be noted that, the proposed model is designed to study gas–liquid interfaces; it is not intended to explore the bulk gas properties and cannot simulate the gas–liquid phase transition.

The proposed DPD method is expected to be efficient for modeling various practical systems, such as bubble suspensions, foams, froths, lipid monolayers, and lung surfactant films to name a few. An immediate important application is screening of environmentally friendly surfactants for flotation separation of minerals,\(^{55} \) as CTAB is considered as a potential candidate for the replacement of traditional surfactants employed in these technologies.\(^{107,108} \)

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.langmuir.0c02572.

Derivation of Gibb’s equation for ionic surfactants; calculation of the critical micelle concentration of CTAB in bulk solution; CTAB surface tension vs surface concentration data from DPD simulations; the details of the MD simulation and the calculation of the octane–gas interfacial density profile; and comparison of theoretical and simulated surface concentrations with neutron reflectivity data (PDF)

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Notes

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