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New Force Field Parameters for the Sodium Dodecyl Sulfate and Alpha Olefin Sulfonate Anionic Surfactants

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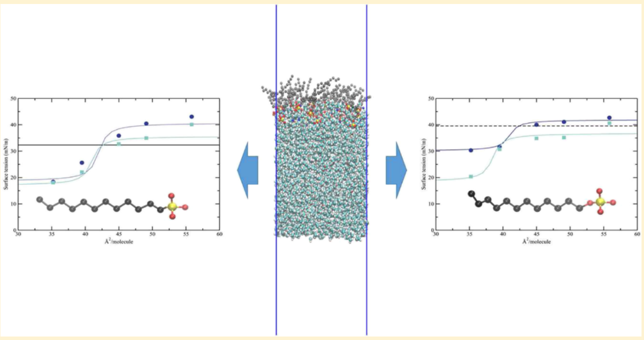
ABSTRACT: Molecular dynamics simulations were carried out to obtain new force field parameters of two most commonly used anionic surfactants: sodium dodecyl sulfate and alpha olefin sulfonate. The present united atom models, of those surfactants, fail to reproduce one of the most important thermodynamic properties, the surface tension. Therefore, by scaling the Lennard-Jones parameters, the potential well (ϵ) and the length (σ), we were able to fit the experimental data. The correct micelle structure of the surfactants was also captured with the new set of parameters. The new proposed united atom models of both surfactants were tested with two different water models, TIP4P/ϵ and SPC/E, and good agreement with actual experiments was found.



1. INTRODUCTION

Studies of surfactants at interfaces have been the subject of several investigations for many years; in particular, from the experimental point of view, several techniques have been used to study different interfacial properties, such as the surface tension.[1−3] On the other hand, computer simulations have also appeared as an alternative to investigate such complex systems. In fact, classical simulations of surfactants with all-atom (AA)[4] and united atom (UA) models[5−15] have been used frequently in the literature. However, to compare simulation results with real experiments, it is important to have good force fields to reproduce correctly dynamical, thermodynamics, and structural properties. Surfactants with AA force fields give, in general, adequate values of the surface tension; unfortunately, those simulations are expensive. A different approach, to conduct those simulations, is the UA models. Most of those force fields capture correctly the structural properties;[16,17] however, they fail to reproduce one of the important thermodynamic properties, the surface tension. In particular, the sodium dodecyl sulfate (SDS) surfactant is one of the common molecules employed in computer simulations;[5,6] however, most of the UA force fields used in the literature do not give correctly the surface tension compared with experimental data.

In the present work, we carried out systematic studies to obtain new force field parameters of two anionic surfactants, the SDS and the alpha olefin sulfonate (AOS) using a UA model, to reproduce the surface tension at the liquid/vapor water interface. Simulations were conducted with two different water models, and good agreement with actual experiments was obtained.

2. COMPUTATIONAL METHOD AND MODEL

For the SDS surfactant, a molecular model of a hydrocarbon chain of 12 united carbon atoms attached to a headgroup, SO_4^-, was used where those atoms were explicitly modeled. For each SDS molecule, a sodium ion (Na^+) was included. For the aqueous phase, two water models, SPC/E[18] and TIP4P/ϵ,[19] were used for the simulations. The SPC/E was selected because it is one of the most common three-site water models used in the literature which reproduces many experimental properties, and it is used in several simulations with surfactants. The TIP4P/ϵ, a four-site water model, was used because it was recently proved to reproduce better several bulk water properties.

The initial configuration was constructed with different numbers of SDS surfactant molecules located in the all-trans conformation, with their headgroups solvated in a water slab with 2500 water molecules. The system was placed in a rectangular box with dimensions $L_X = L_Y = 40.249$ Å, whereas the L_Z dimension of the box was set to 150 Å, that is, there was a water/vapor interface at the end of the system.

Simulations were conducted in the NVT ensemble at constant temperature using the Nosé−Hoover thermostat with a relaxation time constant of 0.5 ps. Another set of simulations were also conducted in a cubic box with a surfactant micelle composed of 60 SDS molecules (the SDS aggregation number[16,17]) embedded in a bulk water phase with 30 000 water molecules. For this case, simulations were carried out in the NPT ensemble at pressure of $P = 1$ bar. The Parrinello−Rahman

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barostat and Nosé–Hoover thermostat were used to maintain the pressure and the temperature constant, respectively, with relaxation times of $\tau_P = 2.0$ ps and $\tau_T = 1.0$ ps.

The total potential contributions in the system are

$$E = E_{\mathrm{bond}} + E_{\mathrm{ang}} + E_{\mathrm{dih}} + E_{\mathrm{LJ}} + E_{\mathrm{Q}} \tag{1}$$

The first three elements correspond to the intramolecular interactions, and the last two correspond to the intermolecular interactions. E_{bond} is the bond potential, E_{ang} is the angle potential, and E_{dih} is the torsional potential. The E_{LJ} term is the Lennard-Jones (LJ) interaction between two atoms, and the E_{Q} term is the Coulombic interaction. For the LJ interactions, the Lorentz–Berthelot mixing rules were used for the unlike atoms.

All simulations were conducted with GROMACS-4.5[20] software using periodic boundary conditions in all directions. The electrostatic interactions were handled with the particle mesh Ewald method, and the short range interactions were truncated at 20 Å. Bond lengths were constrained using the LINCS algorithm, and dispersion corrections were included in the simulations. Then, simulations were performed for 30 ns after 2 ns of equilibration with a timestep of dt = 0.002 ps.

In the AOS system, a hydrocarbon chain of 12 united carbon atoms attached to a headgroup SO_3^-, a similar procedure was conducted, that is, the initial configuration of the surfactants at the liquid/vapor interface and in the micelle was prepared with the same method of the SDS system. For each AOS molecule, a sodium ion (Na^+) was included.

3. OPTIMIZATION PROCEDURE

The methodology to find the optimum parameters of the new force field involves the calculation of a target property, the surface tension. From previous works, it is known that the surface tension can be modified mainly by variations of the ϵ-LJ parameter.[21] Then, the first simulations were conducted for the SDS surfactants with the TIP4P/ϵ water model at the liquid/vapor interface at a temperature of T = 300 K using one of the common force fields reported in the literature.[22] First, the original SDS tail was replaced with a more appropriate hydrocarbon tail, that is, the LJ parameters of the hydrocarbon chains proposed by the de Pablo[23] were used. The parameters given by de Pablo and co-workers were used for the surfactant hydrocarbon tails because those values represent better the behavior of short and large alkane chains at the liquid/vapor interface as they have shown in their paper. In fact, starting from those parameters, the target properties (such as the experimental surface tension) were easier adjusted than with the original parameters.

Then, several simulations of the surface tension were carried out with different ϵ-LJ values, that is, by scaling all values from the original ones, until the calculated surface tension (γ) fits the experimental data within 5% error. Then, with the new ϵ, all σ parameters were scaled to obtain the experimental radius of gyration of the SDS micelle in a bulk water phase. It is worthy to mention that we used the same partial charges reported in the original SDS model in all simulations. For the Na^+ ion, we also kept the same parameters of the original SDS model. Finally, the new SDS force field was tested with a different water model, the SPC/E, and simulations were carried out at different surfactant concentrations and temperatures. For the AOS surfactant, the same procedure was conducted to find the new LJ parameters.

4. RESULTS

4.1. SDS Surfactant. Simulations started with the SDS surfactants and the TIP4P/ϵ water model at the liquid/vapor interface at temperature of T = 300 K. In Figure 1, results of SDS at different areas per molecule (number of SDS molecules) using the original parameters[22] are shown. In the figure, it is possible to observe two regions of the surface tension at low and high areas per molecule, that is, the surface tension undergoes to a drastic change with the SDS concentration. In the same figure, data with the AA model, using CHARMM force field,[4] are also included for comparison. The change in the surface tension could be associated with the surfactant saturation area, for 36 SDS molecules, the surface coverage is 45 Å^2/molecule which is the area per headgroup at the critical micelle concentration at the water/vapor interface.[24] In Figure 2a–d, the density profiles of the systems at different SDS areas per molecule, with the original parameters, are shown. There, the formation of a monolayer is observed where the headgroups are solvated by water, whereas the tail groups are located in the vapor phase; moreover, at low surface coverage (larger number of SDS molecules), above the saturation area, the tail density profiles become wider. However, a more significant difference can be observed in the electrostatic properties at the interface. In Figure 3a–c, electrostatic properties are shown for the systems with the old LJ parameters for the different surface coverage. For those electrostatic calculations, all molecules, the surfactants, the counterions, and water, were used. In the Figure 3c, it is depicted that the electrostatic potential difference decreases with the surface coverage, and it is slightly larger when the surface area changes from 49 to 45 Å^2/molecule.

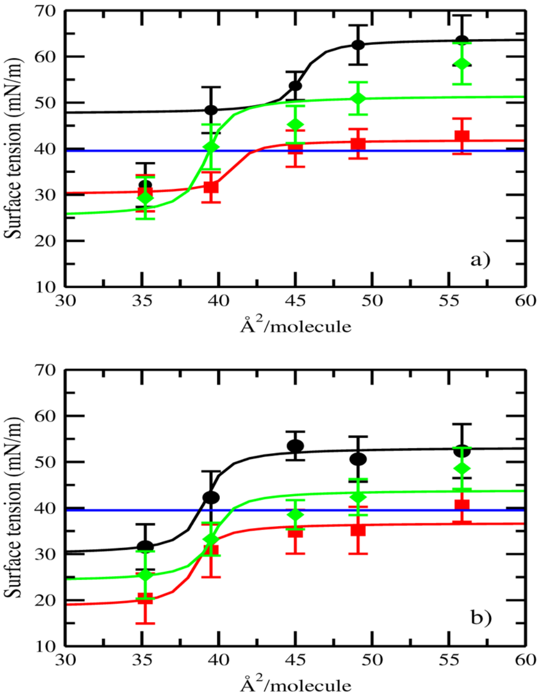

Figure 1. SDS surface tension at the water/vapor interface as a function of the surface area, (a) with TIP4P/ϵ water model and (b) with SPC/E water model. The black data are the results with the old LJ parameters, the red data are the results with the new LJ parameters, and the green data are the results with the AA model. The lines are the best-fitting curves to the points. The experimental value is represented by the blue line.

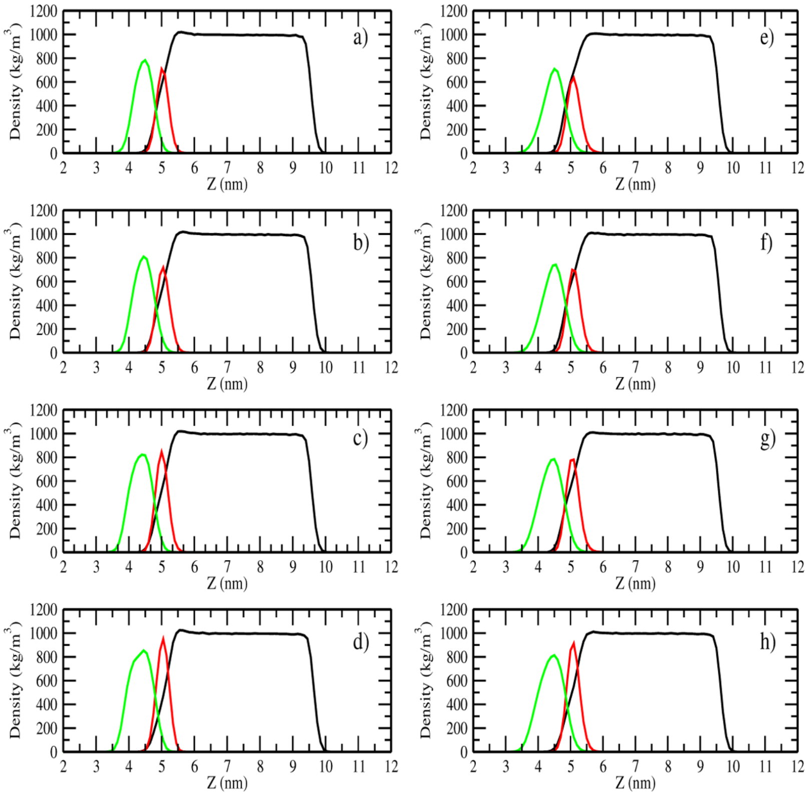

Figure 2. Density profiles of the SDS system at the water/vapor interface with TIP4P/ϵ water. Plots (a,e) at a surface coverage of 49 Å^2/molecule, plots (b,f) at 45 Å^2/molecule, plots (c,g) at 39.5 Å^2/molecule, and plots (d,h) 35.5 Å^2/molecule. Left plots are for the old LJ parameters and right plots are for the new LJ parameters. The black lines represent water, the red lines the SDS headgroups, and the green lines the SDS tail groups.

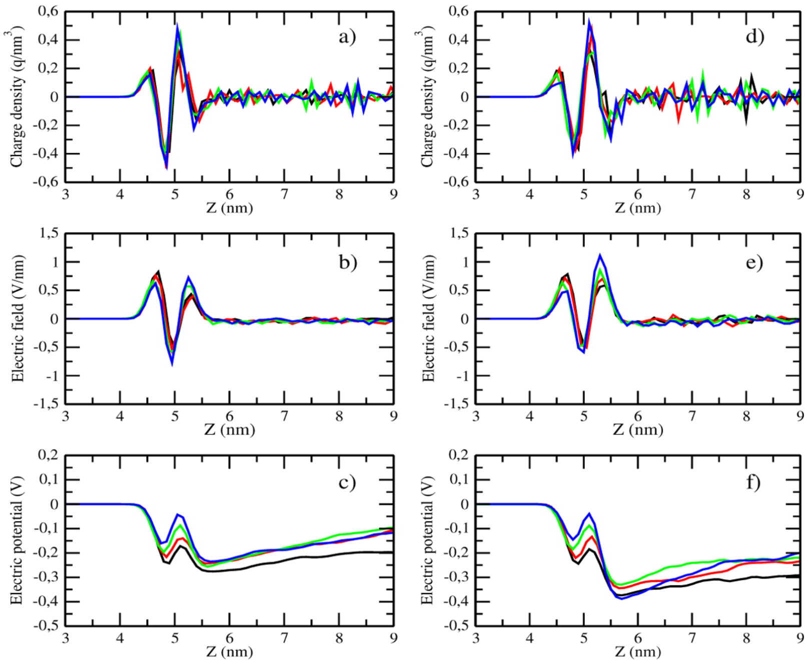

Figure 3. Charge density profiles of the SDS, with TIP4P/ϵ water, at the water/vapor interface, plots (a,d). The electric field, plots (b,e). Electrical potential, plots (c,f). The black lines are the results for the 49 Å^2/molecule, the red lines for the 45 Å^2/molecule, the green lines for the 39.5 Å^2/molecule, and the blue lines for the 35.5 Å^2/molecule. Left plots are for the old LJ parameters, and right plots are for the new LJ parameters.

On the basis of previous results, we took the SDS system at the saturation area, that is, with 36 molecules, to start the parametrization. Then, simulations were conducted by systematically changing the ϵ LJ parameter of all sites in the SDS molecule, from the original values, in increments of 10%, and the surface tension was calculated for each system. Simulations were stopped until the calculated surface tension error was less than 5% with respect to the experimental data.[25,26] The results are given in Table 1. The surface tension was calculated with the mechanical definition for planar interfaces, that is, with the components of the stress pressure tensor, $\Gamma = h[P_{zz} - (P_{xx} + P_{yy})/2]$ with P_{zz} being the normal pressure and P_{xx} and P_{yy} being the tangential pressure. Additional simulations with a larger surface area were also conducted to see any size effects in the calculations. Then, two different systems with 54 and 81 SDS molecules, both with the same surface coverage of 45 Å^2/molecule and with the same ϵ-LJ of 36 SDS, were run to calculate the surface tension. The calculated values for the systems with 54 and 81 SDS had an error of about 2 and 3%, respectively, with respect to the experimental value.

Then, with the new ϵ parameters, simulations at different concentrations were conducted to evaluate the surface tension. A plot similar to that in Figure 1 was obtained for the surface tension as a function of the SDS concentration. Moreover, it also depicted a jump in the surface tension data after the surface coverage of 45 Å^2/molecule, the critical micelle concentration at the water/vapor interface. For comparison, simulations with an AA SDS model were also calculated and plotted in the same figure. For that model, at 45 Å^2/molecule, the simulations give a reasonable value with the experiments.

The density profiles with the parametrized LJ parameters did not change significantly from those calculated previously using the original LJ values (Figure 2e−h). Nevertheless, in this case, the SDS headgroups were more solvated with water molecules. For the electrostatic potential along the interface, it was noted that the potential difference was higher in this case with the new LJ parameters (Figure 3d−f) than that with the original ones.

Simulations of the surface tension at different temperatures were conducted with the new LJ parameters and plotted in Figure 4. From the figure, a linear behavior is observed similar to those indicated in other surfactant systems.[27,28]

With the new parametrized ϵ values, the new σ-LJ parameters were found by fitting a structural property such as the radius of gyration. The procedure to obtain the new σ values was similar to that for the ϵ, the original parameters were scaled in steps of 10% for all atoms in the SDS molecule, and simulations were conducted to calculate the radius of gyration. The results are shown in Table 1, where the best adjustment, without spoiling the surface tension was ≈8% with respect to the experimental value.[29] The new ϵ and σ parameters which reproduce better the experimental values are given in Table 2.

To see if the new ϵ and σ parameters can be transferable to other water models, the same kind of simulations were carried out with the SPC/E water model. In Figure 1b, the surface tension is plotted as a function of the surfactant surface area with the original and new LJ parameters. In this case, it is noted that the plots present an extended plateau before a drastic change is observed compared with the TIP4P/ϵ model. Here, the surface tension, at the surface coverage of 45 Å^2/molecule (36 SDS molecules), gives an error of ≈12%, whereas the radius of gyration has ≈9% error with respect to the experimental values.

It is also possible to determine the number of sodium ions close to the headgroups given by the new model. In Table 3, the fraction of counterions in the first and second shells from the sulfur atoms, calculated from the radial distribution function between the S (sulfur) and Na$^+$ (sodium), is given for all simulations. In the table, it is observed that the distances, with the old parameters, in the first and second shells are nearly the same for all systems and similar to the values reported in previous works.[16] Regardless of the water model, the fraction of Na$^+$ ions close to the SDS headgroups was higher (in the first shell) with

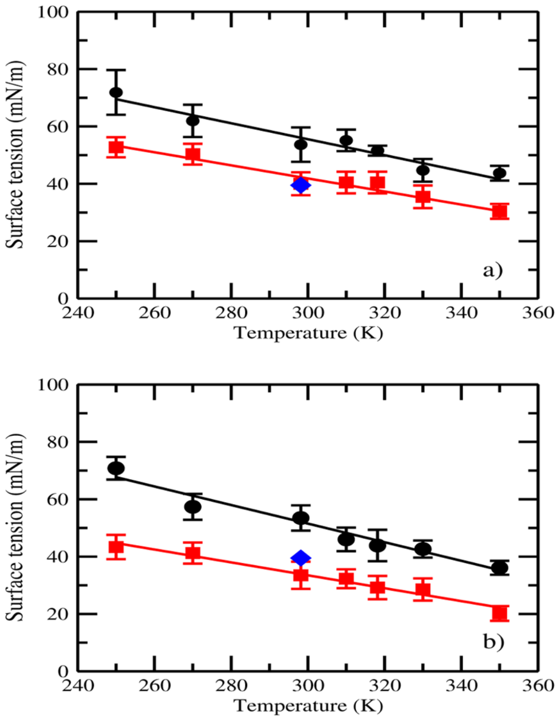

Figure 4. SDS surface tension at the water/vapor interface as a function of the temperature for the surface coverage of 45 Å^2/molecule. (a) Simulations with the TIP4P/ϵ water model and (b) simulations with the SPC/E water model. The black data are the results using the old parameters, the red data are the results using the new parameters, and the blue diamond is the experimental data.

Table 1. Surface Tension of the SDS and AOS Surfactants with Different Water Models[a]

system	surface tension (mN/m)	error (%)	micellar radius (Å)	error (%)
SDS/TIP4Pϵ original	53.6575	35.84	20.86	9.79
SDS/TIP4Pϵ new	40.0045	1.28	20.61	8.47
SDS/SPCE original	53.4795	35.39	20.82	9.58
SDS/SPCE new	34.8298	11.82	20.68	8.84
AOS/TIP4Pϵ original	51.5695	59.46	20.22	6.42
AOS/TIP4Pϵ new	35.8715	10.92	20.05	5.53
AOS/SPCE original	47.9435	48.25	21.79	14.68
AOS/SPCE new	32.7239	1.19	20.01	5.32

[a] The error with the experimental data is given in the table. The experimental surface tension values for the SDS and AOS are 39.5[25,26] and 32.34 mN/m,[30] respectively. The experimental micellar radius is 19.0 Å.[29]

Table 2. SDS Original and New LJ Parameters

site	σ (Å) original	ϵ (kcal/mol) original	σ (Å) new	ϵ (kcal/mol) new
S	3.550	0.2502	3.195	0.175
O(SO$_3$)	3.150	0.2001	2.835	0.140
O(ester)	3.000	0.1701	2.700	0.119
CH$_2$ attached to O	3.905	0.1181	3.537	0.064
CH$_2$	3.905	0.1181	3.537	0.064
CH$_3$	3.905	0.1751	3.519	0.145

Table 3. Fraction of Counterions per Shell Forming Contact Pairs with SDS Headgroups with the Original and New Models with the Different Water Models[a]

force field	distance 1st shell (Å)	distance 2nd shell (Å)	% of counterions 1st shell	% of counterions 2nd shell
SDS/SPCE original	4.28	6.80	36	73
SDS/SPCE new	4.09	6.48	41	74
SDS/TIP4Pϵ original	4.27	6.79	38	73
SDS/TIP4Pϵ new	4.05	6.46	41	73
SDS/TIP3P[16]	4.25	6.80	25	50

[a] The last line are data given in previous works for comparison.[16]

the new SDS model than with the old model. Moreover, the fraction of ions next to the SDS headgroup was higher than that calculated in previous works using a different water model.[16]

4.2. AOS Surfactant. The same procedure and tests were conducted for the anionic surfactant sodium alpha olefin sulfate (AOS). Simulations to calculate the surface tension as function of the surface coverage are shown in Figure 5. To the best of our knowledge, for this system, we did not find any reported critical micelle concentration at the water/vapor interface. From the figures, it is possible to observe a jump after the value of the surface coverage of 45 Å^2/molecule. Because the AOS has a structure similar to that of the SDS molecule, we expected a similar surface coverage at saturation. Therefore, the reparametrization of the ϵ parameter started at the surface coverage of 45 Å^2/molecule (36 AOS molecules) with the original parameters given in ref 7. As for the SDS system, the new ϵ parameters were found by conducting simulations with the TIP4P/ϵ water model and by scaling the parameters to obtain the best fit with the experiments. In this case, we found an error of ≈11% with respect to the experimental data;[30] nevertheless, this value was much better than the one obtained with the original parameters, see Table 1. As for the SDS, simulations of an AOS micelle in bulk water were conducted to find the new σ parameters. Several simulations were carried out by changing the σ parameters from the original ones, and the radius of gyration was evaluated. Here, the best fit with the experiments did not improve significantly the micellar radius as indicated in Table 1. The new ϵ and σ parameters for the AOS surfactant are given in Table 4. In Figure 6, the density profiles of the AOS monolayer at the water/vapor interface at different surface coverages are shown. A similar behavior as in the SDS system was observed. In Figure 7, electrostatic properties are also shown, and it is observed that the electrostatic potential difference also decreases with the surface coverage. Moreover, in this case, the differences in the electrostatic potential are lower than those in the SDS system.

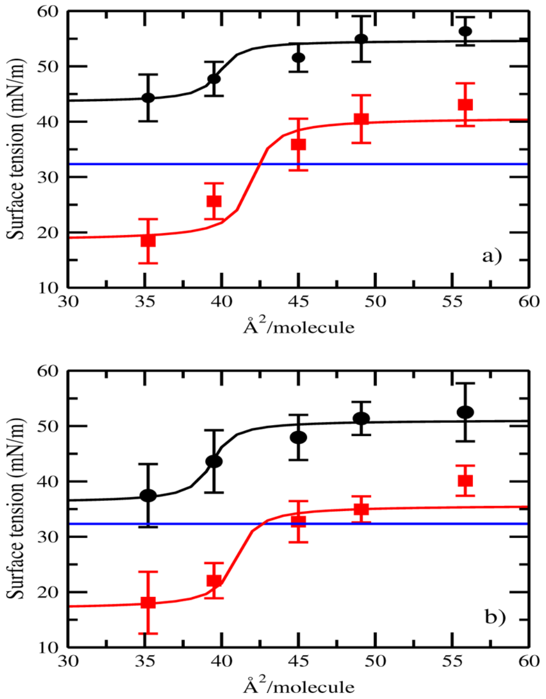

Figure 5. AOS surface tension at the water/vapor interface as function of the surface area, (a) with TIP4P/ϵ water model and (b) with SPC/E water model. The black data are the results with the old LJ parameters and the red data are the results with the new LJ parameters. The lines are the best-fitting curves to the points. The experimental value is represented by the blue line.

Table 4. AOS Original and New LJ Parameters

site	σ (Å) original	ϵ (kcal/mol) original	σ (Å) new	ϵ (kcal/mol) new
S	3.550	0.2502	3.195	0.213
O(SO$_2$)	3.150	0.2001	2.835	0.170
O(ester)	3.000	0.1701	2.700	0.145
CH$_2$ attached to S	3.905	0.1181	3.515	0.100
CH$_2$ double bond	3.770	0.0914	3.393	0.078
CH$_2$	3.905	0.1181	3.537	0.077
CH$_3$	3.905	0.1751	3.519	0.176

Simulations of the AOS monolayer at the water/vapor interface with the SPC/E water model were also conducted using the new ϵ and σ LJ parameters. Once again, a jump was observed in the surface tension as a function of the AOS concentration after the surface coverage of 45 Å^2/molecule. In this case, the error in the surface tension was less than 1% with respect to the experimental data, that is, simulations with the SPC/E model gave a better agreement with the experimental value than that with the TIP4P/ϵ model. The radius of gyration of an AOS micelle in a bulk water phase was also calculated and compared with the experiments. Here, the value of the micelle radius was very similar to that found with the TIP4P/ϵ model .

Calculations of the surfactant tension at different temperatures were also carried out with both water models, and nearly a linear behavior was observed as shown in Figure 8.

4.3. Conclusions. Computer simulations of the water/surfactant/air interface were carried out to calculate a new set of LJ parameters for the force field of two anionic surfactants with a UA model, the SDS and the sodium AOS. Previous models of both surfactants, with UA models, did not reproduce correctly the experimental surface tension, that is, those models failed to capture one of the most important thermodynamic properties of the surfactants. The new ϵ-LJ parameters were determined by scaling all old values until the task property, the surface tension, was obtained. Structures of the surfactants, such as micelles, were used to correct the other LJ parameter, σ, and good agreement was found with the experiments.

It is worthy to mention that AA models of the SDS produce suitable surface tensions; however, simulations with those

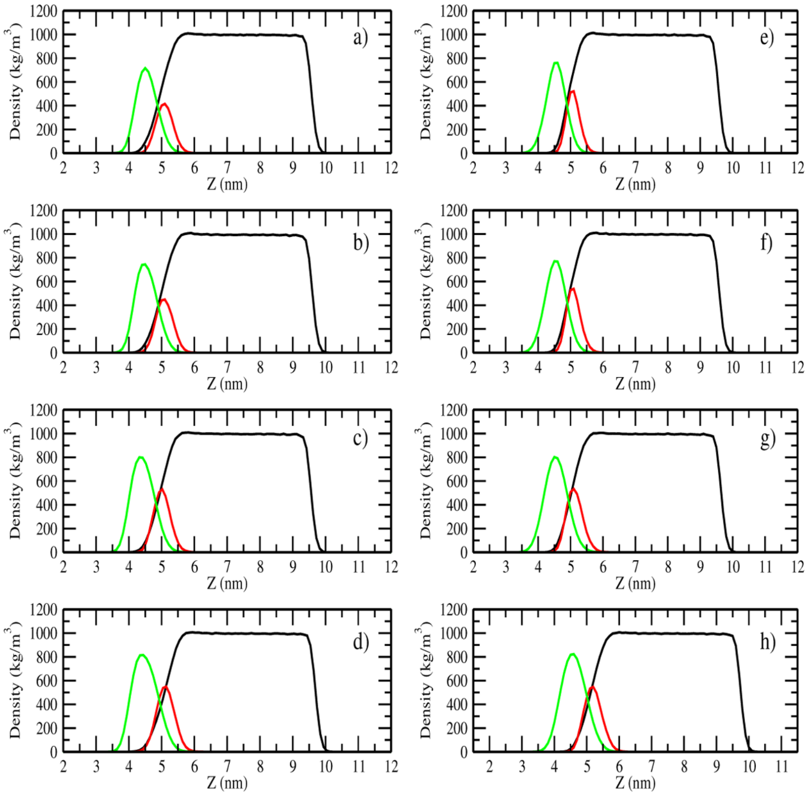

Figure 6. Density profiles of the AOS system at the water/vapor interface with TIP4P/ϵ water. Plots (a,e) at a surface coverage of 49 Å^2/molecule, plots (b,f) at 45 Å^2/molecule, plots (c,g) at 39.5 Å^2/molecule, and plots (d,h) at 35.5 Å^2/molecule. Left plots are for the old LJ parameters and right plots are for the new LJ parameters. The black lines represent water, the red represent lines the SDS headgroups, and the green lines represent the AOS tail groups.

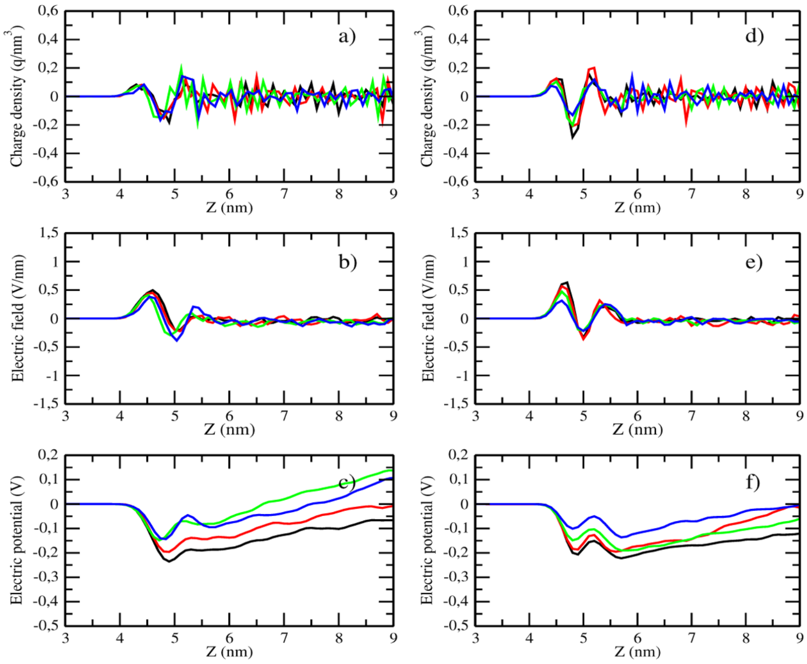

Figure 7. Charge density profiles of the SDS, with TIP4P/ϵ water, at the water/vapor interface, plots (a,d). The electric field, plots (b,e). Electrical potential, plots (c,f). The black lines are the results for the 49 Å^2/molecule, the red lines are the results for the 45 Å^2/molecule, the green lines are the results for the 39.5 Å^2/molecule, and the blue lines are the results for the 35.5 Å^2/molecule. Left plots are for the old LJ parameters, and right plots are for the new LJ parameters.

models are expensive. Therefore, it is convenient to have reliable UA models to conduct good simulations to study interfacial properties. In the present work, we have proposed new parametrized force fields of the SDS and AOS surfactants which reproduced correctly the surface tension and the radius of the micelles. Simulations were tested with two different water

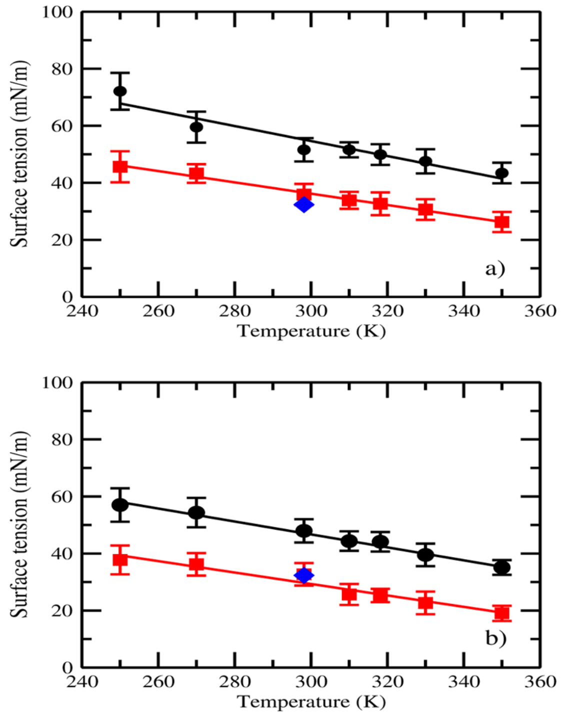

Figure 8. AOS surface tension at the water/vapor interface as a function of the temperature for the surface coverage of 45 Å^2/molecule. (a) Simulations with the TIP4P/ϵ water model, (b) simulations with the SPC/E water model. The black data are the results using the old parameters, the red data are the results using the new parameters, and the blue diamond is the experimental data.

models, three-site and four-site models, and good agreement with experimental data was found.

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Notes

The authors declare no competing financial interest.

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