

Computer Simulations of Catanionic Surfactants Adsorbed at Air/Water Interfaces

Javier Rodriguez,^{†,‡} Esteban Clavero,[†] and Daniel Laria^{*,†,‡}

Departamento de Química Inorgánica, Analítica y Química-Física e INQUIMAE, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Ciudad Universitaria, Pabellón II, 1428 Buenos Aires, Argentina, and Unidad Actividad Química, Comisión Nacional de Energía Atómica, Avenida Libertador 8250, 1429 Buenos Aires, Argentina

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Structural properties pertaining to the solvation of mixtures of dodecyltrimethylammonium/dodecylsulfate adsorbed at water/air interfaces were studied using molecular dynamics techniques. Two different surfactant coverages, both in the submonolayer regime, were considered: an infinite-diluted catanionic pair and an equimolar mixture, at a surface concentration of 78.7 Å²/headgroup. The most stable solvated structures for the single surfactant pair correspond to contact-head-ion-pairs (CHIP) at a distance close to 5 Å. In addition, marginally stable solvent-separated-head-ion-pairs (SSHIP) at distances ~ 7 Å were also observed. The mean free energy for the dissociation of CHIP was estimated to be ~ 1 kcal/mol. At finite surfactant concentrations, one observes a considerable degree of clustering between the amphiphiles, due to the strong Coulomb coupling between headgroups. The resulting spatial domains show asymmetric structures with linear dimensions comparable to the simulation box, suggesting the onset of percolative structures. The connectivity pattern of these domains was interpreted in terms of a simplified model consisting of two-dimensional charged Lennard–Jones spheres.

I. Introduction

The subject of chemical reactivity at interfaces continues to draw considerable attention from both experimental and theoretical perspectives.^{1,2} Its relevance resides in the important modifications that operate in the reactive channels of most processes, when compared to what is perceived in isotropic phases. In all these cases, the origin of these modifications can be traced back to changes in the original bulk structure, that take place over lengthscales which are comparable to typical molecular sizes. Without being exhaustive, the list of phenomena we are referring to includes (i) large gradients in density and polarization fields,³ (ii) modifications of intermolecular connectivity,⁴ (iii) “unusual” fluctuations of local concentrations of different chemical species,⁵ and (iv) large unbalances in the forces that drive the dynamics of adsorbed species.⁶

Liquid/air interfaces represent environments of primary interest since they host reactive processes of fundamental importance in many areas of chemistry. Environmental chemistry is one clear example: phenomena such as the mass transport of species into aerosol droplets, the adsorption of pollutants, the release of halogens into the atmosphere, and the heterogeneous formations of clouds are controlled by reactions at liquid/air interfaces. Furthermore, the adsorption of amphiphilic species opens new and interesting possibilities to expand the universe of interfacial environments into a new series of scenarios with distinctive characteristics. Perhaps one of the most important appeals of the latter systems is given by the fact that they have incorporated functional groups also present in more complex supramolecular assemblies, such as micelles, lipidic bilayers, vesicles, and cell membranes.⁷

The present paper deals with the solvation of mixed ionic surfactants adsorbed at air/water interfaces. From a practical point of view, the analysis of such systems is of particular relevance since most technological and commercial application of tensioactives rely on the use of surfactant blends, involving ionic and/or nonionic species as well. More specifically, we will focus attention on catanionic surfactants. These amphiphilic molecules can be considered to be salts of an anionic and a cationic surfactant, and they are akin to equimolar mixtures of ionic surfactants of opposite charge. In fact, a large body of experimental results seems to suggest that many physicochemical properties of the latter mixtures are only slightly dependent on the explicit presence of counterions in the aqueous phase.^{8–10} One particular feature distinguishes catanionic surfactants from other surfactant mixtures: the strong Coulomb interactions between oppositely charged headgroups. The characteristics of this coupling are, in turn, translated into changes in critical aggregation concentrations, larger detergency activities, and the possibility of generating new microstructures such as vesicles or rodlike micelles.^{11–13}

Although catanionic surfactants have been intensively studied by a variety of experimental techniques,^{14–19} a detailed microscopic description of their solvation structures is still lacking. From the theoretical point of view, there have been previous efforts to predict their thermodynamic properties, most notably those based on classical theories of liquid mixtures.^{20–23} However, with the exception of some recent molecular dynamics studies of mixed ionic–nonionic mixtures of adsorbed surfactants,²⁴ we know of no previous work focused on mixtures of charged surfactants from a computer simulation perspective. In an effort to shed light on the microscopic details pertaining to the solvation of these complex systems, we present molecular dynamics results for surface states of equimolar mixtures of dodecyltrimethylammonium/dodecylsulfate. Previous studies

* Corresponding author. E-mail: dhlaria@cnea.gov.ar.

[†] Universidad de Buenos Aires.

[‡] Comisión Nacional de Energía Atómica.

have analyzed the separate adsorption of similar surfactants in the presence of aqueous counterions,^{25,26} covering different regimes of surface concentrations. In this initial exploratory step, we started by considering two systems, both in the regime of low surfactant coverage: first, the simplest case of an infinitely diluted surfactant pair and, second, a surface coverage that would correspond to approximately one-third of a saturated monolayer. Our interest here was centered on the structural features of the solvated surfactants and the aqueous substrate. In addition, we provide a few indications of dynamical characteristics of the adsorbed species as well. This paper is organized as follows: Details of the simulation procedure and models are described in section II. The main results for catanionic pairs and low surface coverages are presented in sections III and IV, respectively. Our concluding remarks appear in section IV.

II. Model and Simulation Procedure

Simulation experiments were performed on systems containing similar amounts of cationic and anionic surfactants adsorbed at one of the liquid/air interfaces of an aqueous slab. The slab was generated from a fully periodic system of linear dimensions $28.06 \times 28.06 \times 24.95$ Å, in which periodic boundary conditions were suppressed along the shortest axis of the simulation box (hereafter referred to as the z -axis). The total number of water molecules was set to $N_w = 648$. After an equilibration period of 100 ps, an equal number N_s of dodecyl-sulfate (DS) $[\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^-]$ and dodecyltrimethylammonium (DTA) $[\text{CH}_3(\text{CH}_2)_{11}\text{N}(\text{CH}_3)_3^+]$ ions was distributed, with their headgroups in the vicinity of one of the slab interfaces. The initial intramolecular geometries of both surfactants corresponded to fully *trans* conformers, with their head-to-tail vectors oriented mostly perpendicular to the interface. Two different surface coverages were analyzed: first, the simplest case of an infinitely diluted surfactant pair and, second, an electrically neutral mixture containing five ion pairs. Under these circumstances, the resulting surface area per headgroup was $\rho_s^{-1} = 78.7$ Å²; this coverage corresponds to approximately one-third of the full monolayer experimental value.¹⁸

Water molecules were modeled using the simple point charge (SPC) model.²⁷ For both surfactants, we used a fully flexible model Hamiltonian that included stretching, bending, and dihedral contributions. Using the united atom description for CH₂ and CH₃ groups, DS and DTA molecules comprised a total of 17 and 16 interaction sites, respectively. Length and energy parameters for inter- and intramolecular potentials corresponded to the GROMACS force field;²⁸ partial charges were taken from a Merz–Kollman–Singh analysis²⁹ at the semiempirical AM1 level of approximation.³⁰ Intramolecular constraints in water molecules were handled by the RATTLE algorithm,³¹ while long-ranged Coulomb interactions were treated using Ewald summation techniques using a particle mesh procedure adapted for slab geometries (the final boxlength in the z direction was set to 100 Å).³² The dynamical trajectories corresponded to microcanonical runs at temperatures close to $T \approx 298$ K. In this temperature regime, the slabs presented stable structures, with negligible evaporation. Production runs were preceded by a second thermalization run of 500 ps, in which only the surfactant tails were allowed to move at $T \sim 700$ K; after that, the systems were gradually cooled to ambient temperature, during a subsequent time interval of 250 ps. Meaningful statistics were collected along equilibrium trajectories of ~ 5 ns.

III. Single Catanionic Surfactant Pair

A. Density Profiles and Surfactant Structures. We will start our analysis by investigating the characteristics of the density

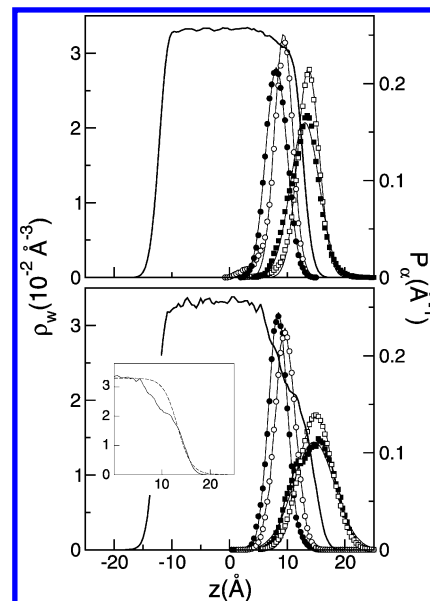


Figure 1. Water local density (thick solid lines, left axis) and probability densities (right axis) for the surfactants. The top panel corresponds to an infinitely diluted surfactant pair; the bottom panel correspond to a surface concentration of $\rho_s^{-1} = 78.7$ Å². Head and tail distributions are shown as circles and squares, respectively. Black and white symbols correspond to DTA and DS, respectively. Also shown are fits from eq 2 (thin solid lines) and eq 3 (dashed line).

fields associated with a set of relevant chemical species. In the top panel of Figure 1, we present results for the z -dependent water density, namely, the number of water molecules per unit of area in the xy -plane, A , with their oxygen sites lying between z and $z + dz$:

$$\rho_w(z) = \frac{1}{A} \left\langle \sum_{i=1}^{N_w} \delta(Z_i - Z_{\text{CM}} - z) \right\rangle \quad (1)$$

In the previous equation, $\langle \dots \rangle$ denotes an equilibrium ensemble average, while Z_i and Z_{CM} represent the z -coordinates of the i th water oxygen and the center of mass of the water slab, respectively. In the same figure, we have also included results for the density profiles of the surfactant species. In this case, we discriminated headgroup (HD) from tail (TL) contributions. For each surfactant (DS and DTA), the quantities of interest are of the following type:

$$P_\alpha(z) \propto \left\langle \sum_i \delta(z_i^\alpha - Z_{\text{CM}} - z) \right\rangle \quad (2)$$

where z_i^α represents the z -coordinate of the i th site lying in the α portion of the surfactant molecule ($\alpha = \text{HD}$ or TL). Tail distributions included contributions from the 12 C sites, while head distributions included the rest of the surfactant sites, i.e., the $-\text{OSO}_3^-$ group for DS and the $-\text{N}(\text{CH}_3)_3^+$ group for DTA.

For the case of water, the density decay at the right-hand side interface can still be reasonably well described by predictions from standard mean-field theories:³³

$$\rho_w(z) \sim \frac{\rho_b}{2} \left[1 - \tanh \frac{z - \bar{z}_w}{\Delta z_w} \right] \quad (3)$$

where ρ_b represents the water bulk density. Using this model, the resulting width of the interface was $\Delta z_w = 1.72$ Å. A similar estimate was obtained using an alternative criterion based on the position of the z -coordinates at 10% and 90% of ρ_b . This

TABLE 1: Solvation Parameters for the Superficial Solvation of Catanionic Surfactants

	N_s	δ_{HD} (Å)	δ_{TL} (Å)	σ_{HD} (Å)	σ_{TL} (Å)	$\langle \cos \theta_{tl} \rangle$	$\langle r_{tl} \rangle$ (Å)
DS	1	-3.3	1.0	4.4	5.2	0.33	10.9
	5	-2.6 ^a	3.0 ^a	5.2	8.0	0.55	13.2
DTA	1	-4.5	0.4	5.2	7.2	0.48	10.9
	5	-3.6 ^a	2.7 ^a	5.2	10.0	0.70	11.0

^a Computed from the position of the Gibbs dividing surface.

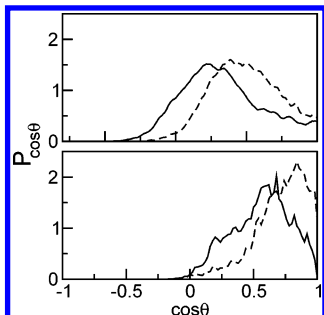


Figure 2. Distributions for the tail tilts of catanionic surfactants. Solid and dashed lines correspond to DS and DTA, respectively: (top panel) infinitely diluted surfactant pair; (bottom panel) $\rho_s^{-1} = 78.7 \text{ Å}^2$.

value should be compared to that obtained from a fit performed on the left-hand side profile, corresponding to the clean interface, $\Delta z_w = 1.40 \text{ Å}$. As expected, the presence of an isolated surfactant pair introduces only minor effects in the overall roughness of the interface. Of course, changes in the width, as reflected by the average of eq 1, are finite size effects and should fade away as one considers larger samples, since the modifications are restricted to the local aqueous environment in the close vicinity of the surfactants.

Normalized head and tail distributions for both surfactants exhibit Gaussian-like profiles of the following type:

$$P_\alpha(z) \sim \left(\frac{4}{\pi \sigma_\alpha^2} \right)^{1/2} \exp \left[-\frac{4(z - \bar{z}_\alpha)^2}{\sigma_\alpha^2} \right] \quad (4)$$

Values for the relative positions $\delta_\alpha = \bar{z}_\alpha - \bar{z}_w$ and the widths σ_α of the Gaussian distributions are presented in Table 1. One observes that the average positions of the DTA and DS headgroups are shifted 4.5 and 3.3 Å, respectively, toward the bulk region. On the other hand, the positions of the corresponding hydrophobic tails are slightly displaced (0.4–1 Å) in the opposite direction. We remark that this trend is accordant with experimental evidence obtained from neutron reflectivity experiments performed on nonsymmetric surfactant mixtures of *n*-hexylammonium and *n*-dodecylsulfate, that show a larger degree of penetration of the cationic surfactant compared to that exhibited by the anionic one.^{16,34}

Concerning the solvation of the hydrophobic portions of the surfactants, in the top panel of Figure 2, we present results for the distributions of tail tilts, $\cos \theta_{tl}$. This quantity represents the cosine of the angle between the tail end-to-end vector \mathbf{r}_{tl} and the *z*-axis. For the sake of completeness, average values of the distributions and $\langle r_{tl} \rangle$ are also presented in the last two columns of Table 1. The lengths of the hydrophobic tails of both surfactants are similar, $\langle r_{tl} \rangle \sim 11 \text{ Å}$, which corresponds to conformations with, typically, ~ 1 – 3 randomly distributed, *gauche* bonds.

On the other hand, tilt distributions look different, the one for DS being somewhat broader than that for DTA, which also includes sizable contributions from $\cos \theta_{tl} < 0$. The average orientation of the DTA tail with respect to the *z*-axis is $\theta_{tl} \sim$

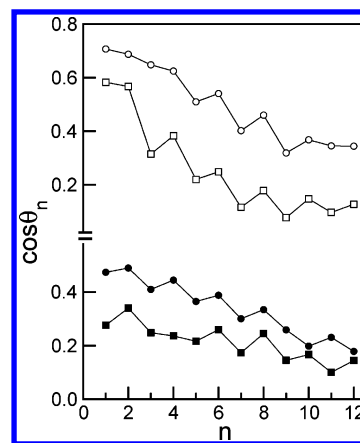


Figure 3. Average orientation of C–C bonds for catanionic surfactants. White symbols correspond to infinitely diluted surfactant pairs; black symbols correspond to $\rho_s^{-1} = 78.7 \text{ Å}^2$. Squares and circles correspond to DS and DTA, respectively.

60° , while the SDS molecule shows more tendency to a parallel orientation with respect to the plane of the interface, $\theta_{tl} \sim 70^\circ$.

The tails for both surfactants being of similar length and presenting identical intramolecular and intermolecular interactions, we are led to believe that the differences in the observed tilts are likely to be originated in their articulations with the solvated headgroups. At these low surfactant concentrations, we remark that the overall orientations of the tails are the result of an interplay between intramolecular interactions dictated by *gauche*–*trans* equilibria and the interactions with the aqueous substrate. To analyze this point in more detail, we investigated local inclinations of the individual C–C bonds. We focused attention on $\cos \theta_n$ ($n = 2, 3, \dots, 12$), where θ_n represents the angle between the C_n – C_{n-1} bond and the *z*-axis (the labeling of C_n groups is such that the CH_2 group closest to the headgroup corresponds to C_1 , while the distal CH_3 group corresponds to C_{12}). Results for $\langle \cos \theta_n \rangle$ are presented in Figure 3; also included are the results of $\langle \cos \theta_1 \rangle$, the orientation of the HD–TL articulation bonds, i.e., O– C_1 and N– C_1 for DS and DTA, respectively. Local orientations of the two surfactants are qualitatively different: While in DTA there is a gradual transition from mostly perpendicular ($1 \leq n \leq 5$) toward more parallel ($n \geq 6$) alignments, the hydrophobic tail of DS presents a clear “break” at the C_1 – C_2 – C_3 region, as $\cos \theta_n$ drops from ≈ 0.6 down to 0.3. The location of this net bend separating the “penetrating” from the “protruding” portions of the molecule, practically coincides with that of the Gibbs dividing surface.

B. Surface Solvation of Catanionic Pairs. To explore deeper into the nature of the surface states of catanionic pairs, we also monitored the temporal dependence of a selected set of physical observables. The first parameter that we studied was the distance between headgroups. In Figure 4, we present results for the time evolution of $r_{NS} = |\mathbf{r}_N - \mathbf{r}_S|$, where \mathbf{r}_α represents the coordinate of site α . The plot includes results collected along a fairly long, 5 ns, trajectory. During this time span, bound surfactant headion-pairs at a distance $r_{NS} \sim 5 \text{ Å}$ are easily identified, as are the episodes of dissociation taking place at characteristic time scales on the order of 0.2–0.5 ns. The magnitude of the observed time scales characterizing the interconversions, suggests the presence of a high activation barrier (compared to normal thermal energies) along the reaction path that connects associated and dissociated pair states.

Several techniques have been devised to compute the magnitude of high free energy barriers separating reactant and product states. Two widely used approaches are based on non-

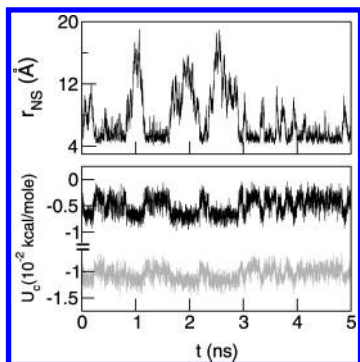


Figure 4. (top panel) Time evolution of the N–S distance of a single catanionic surfactant pair. (bottom panel) Time evolution of the DS (gray line) and DTA (black line) Coulomb couplings with the aqueous substrate (contributions from water molecules located beyond 10 Å of the headgroups were disregarded).

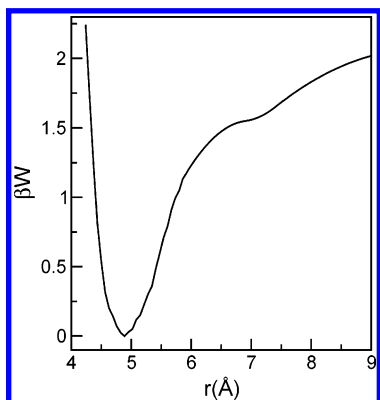


Figure 5. Potential of the mean force for the dissociation of an adsorbed catanionic pair at infinite dilution.

Boltzmann sampling³⁵ and on constrained dynamics techniques.³⁶ In addition, new alternative strategies have been recently devised, based on sampling an ensemble of properly weighted reactive paths.³⁷ The implementation of the former schemes normally requires an a priori guess of a reaction coordinate. For this particular case, we can anticipate that such identification is far from being straightforward: In principle, a natural choice would be the consideration of some relevant length scale, such as r_{NS} . However, dissociation paths for the head-ion-pair are likely to be triggered, in part, by fluctuations involving a manifold of degrees of freedom (including head and tail coordinates as well). Moreover, we cannot discard the fact that the dissociation mechanism might also be regulated by fluctuations involving the interfacial substrate. In passing and to provide evidence of the latter assertion, in the bottom panel of Figure 4, we present results for the time evolution of the Coulomb coupling between both headgroups and the water substrate. One can easily correlate dissociation/association episodes to concomitant larger/smaller Coulomb coupling intervals.

Despite these drawbacks and even though we might not be capturing the complete set of relevant fluctuations that drive the dissociation/association process of the surfactant pair, we tried to obtain a rough estimate of the order of magnitude of the free energy barrier associated with the dissociation process by resorting to constrained dynamics. We computed the mean free energy profile by integrating mean forces $F(r)$ acting on the N and S sites, calculated at selected constrained distances r for the N–S pair.³⁶ The results are depicted in Figure 5: The curve shows a minimum at $r = 4.9$ Å, corresponding to contact-head-ion-pairs (CHIP), and an intermediate flatter region for r

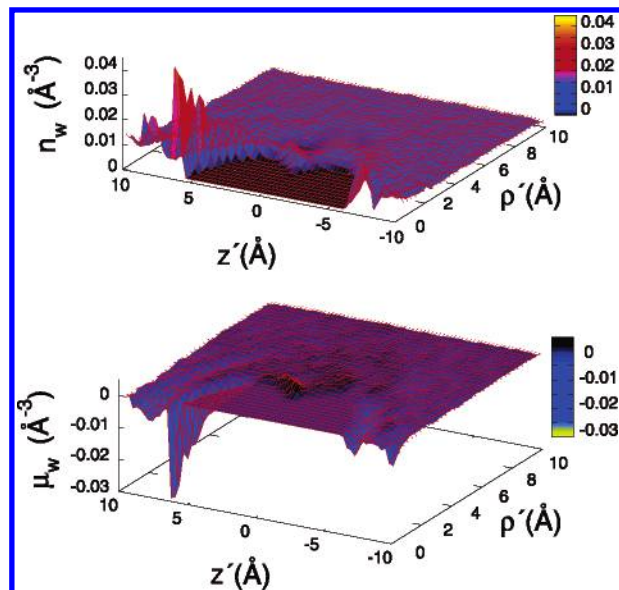


Figure 6. Solvent number (top panel) and polarization (bottom panel) densities for the vicinity of an infinite-diluted adsorbed contact-ion-head-pair, $r_{NS} = 4.9$ Å.

~ 7 Å, corresponding to marginally stable solvent-separated-head-ion-pairs (SSHIP). The free energy barrier for the CHIP \rightarrow SSHIP transition is $W^\ddagger \sim 1.5k_B T$. Incidentally, note that the magnitude of this barrier would yield a transition state theory (TST) estimate for the rate of dissociation, $k_{TST} \sim (\beta h)^{-1} \exp(-\beta W^\ddagger) \sim 1$ ps⁻¹, which is at odds with the much longer dissociation time intervals perceived from the time evolution of r_{NS} shown in Figure 6.

In the present context, we are led to believe that such discrepancy is the result of the strong coupling that exists between the proposed reaction coordinate and the manifold of degrees of freedom involving not only the substrate but, more importantly, the head and tail sites, via strong intramolecular bonds.³⁸

Additional details pertaining to the solvation of surfactant pairs can be obtained by inspecting spatial and polarization density profiles for the solvent lying in the close vicinity of the interface. To analyze the distribution of neighboring water molecules, we considered a local system of coordinates (x' , y' , z') centered at the midpoint between the N and S sites. Exploiting the cylindrical symmetry of the system around the axis joining the headgroups, one can define appropriate distribution functions along z' and ρ' . The z' direction coincides with that of $\mathbf{r}_N - \mathbf{r}_S$ and $\rho' = \sqrt{x'^2 + y'^2}$; x' and y' are arbitrarily chosen directions, and both are orthogonal to z' . Armed with these definitions, we computed normalized number $n_w(r, \rho')$ and dipolar $\mu_w(r, \rho')$ densities for water according to

$$n_w(\rho', z') = \frac{1}{2\pi\rho'} \left\langle \sum_i H(z_i - z_0) \delta(\rho'_i - \rho') \delta(z'_i - z') \right\rangle \quad (5)$$

and

$$\mu_w(\rho', z') = \frac{1}{2\pi\rho'} \left\langle \sum_i \frac{\boldsymbol{\mu}_i \cdot \mathbf{z}'}{|\boldsymbol{\mu}_i|} H(z_i - z_0) \delta(\rho'_i - \rho') \delta(z'_i - z') \right\rangle \quad (6)$$

In the previous equation, $\boldsymbol{\mu}_i$ represents the dipole moment of the i th water molecule, \mathbf{z}' is the unit vector along the z' direction, and $H(z)$ represents the Heaviside function that filters out

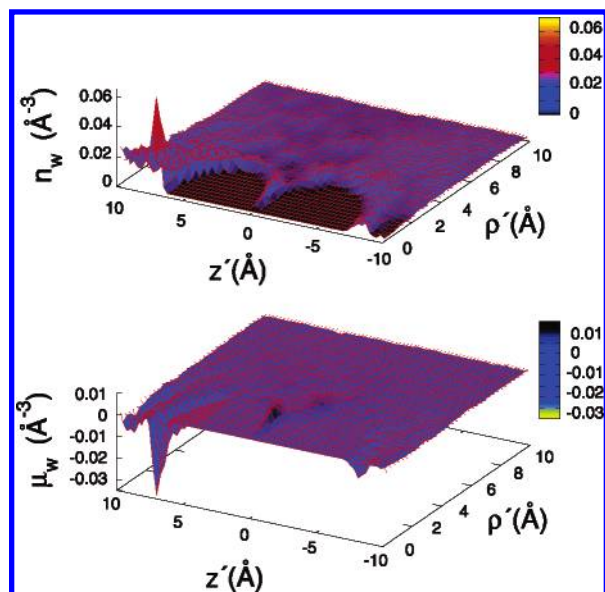


Figure 7. Same as Figure 6 for a solvent-separated-ion-head-pair, $r_{\text{NS}} = 7 \text{ \AA}$.

contributions from those molecules whose z -coordinates are less than a threshold value that was set at $z_0 = 11 \text{ \AA}$. The number of water molecules included in this set is approximately 60. In Figures 6 and 7, we present results for the densities obtained from trajectories in which the distance between the headgroups was constrained at typical values of CHIP and SSHIP, $r_{\text{NS}} = 4.9$ and 7 \AA , respectively. The overall solvation structure of adsorbed head-ion-pairs is asymmetric and mainly localized in the axial regions, $7 \text{ \AA} \lesssim |z'| \lesssim 10 \text{ \AA}$. Due to the stronger Coulomb coupling between the DS headgroups and the substrate—already shown in the bottom panel of Figure 4—density and dipolar local fluctuations around the negatively charged portion of the adsorbed moiety are larger than in the vicinity of the DTA group. Bridging the gap between the headgroups, we observe the presence of tightly bound water molecules, with the opposite polarization to that observed at the axial regions. Although this feature is barely perceptible for $r_{\text{NS}} = 4.9 \text{ \AA}$, it becomes self-evident for $r_{\text{NS}} = 7 \text{ \AA}$ and includes a number of wedged water molecules close to ~ 2 , a description that brings support to the SSHIP acronym given above.

IV. Adsorption at Finite Surface Coverages

In this section, we analyze the solvation of catanionic surfactants at a finite surface concentration of $\rho_s^{-1} = 78.7 \text{ \AA}^2$. To facilitate the comparison with the isolated pair case, the density profiles at these new conditions are shown in the bottom panel of Figure 1. At a first glance, the clearest differences between both sets of results are found in the shapes of the solvent density decay profiles. The presence of larger amounts of charged surfactants considerably modifies the width of the interface. An estimate based on the positions of the z -coordinates at 10% and 90% of ρ_b yields a value of $\Delta z_w = 9.7 \text{ \AA}$, practically five times larger than in the previous case. For $6 \text{ \AA} < z < 11.5 \text{ \AA}$, the water profile looks somewhat steeper and differs considerably from the usual hyperbolic tangentlike shape (see the inset in the figure). In the more external portion of the interface ($z > 12 \text{ \AA}$), the density decay recovers the smoother character of clean interfaces. Interestingly, note that the first region coincides with the location of the headgroups, which still lie $\sim 3 \text{ \AA}$ inward to the position of the Gibbs dividing surface (see entries in Table 1). The data of Table 1 also show a

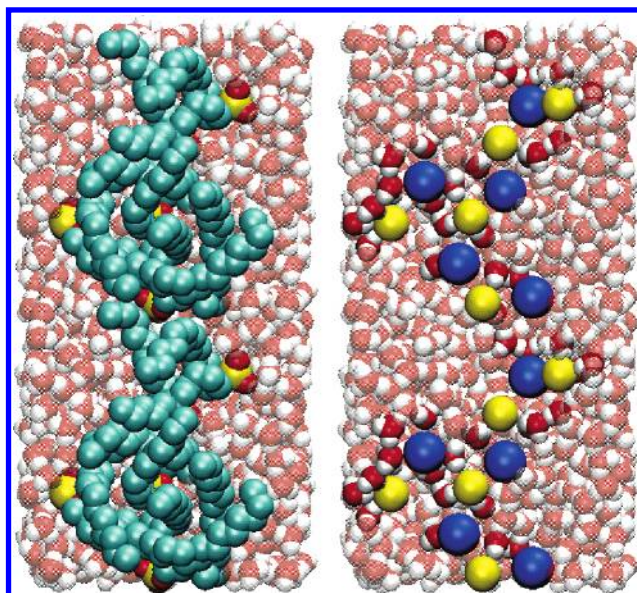


Figure 8. (left panel) Snapshot for a typical configuration of an adsorbed mixed catanionic surfactant at $\rho_s^{-1} = 78.7 \text{ \AA}^2$. To allow a more clear perception of the asymmetric structure of the surfactant domain, the simulation box has been replicated along the vertical direction. (right panel) Layout of adsorbed headgroups for the same configuration as the one shown in the left panel (for clarity purposes, only N and S are shown). Water molecules in the close vicinity of the surfactant headgroups are highlighted. S and N groups are depicted as yellow and blue spheres, respectively.

moderate enlargement of the widths of the Gaussian distributions for the tails of both surfactants. As expected, interactions between the hydrophobic tails shift their overall orientations toward perpendicular alignments with respect to the plane of the interface. The entries in Table 1 show that this tendency is more marked for DTA than for DS. From the bottom panel of Figure 3, also note that fluctuations in the overall orientations become smaller and that the contributions from $\cos \theta_{\text{il}} < 0$ have practically disappeared for the DS tilt distribution. Local orientations of the individual C—C bonds show modifications which are accordant with the observed overall values of $\langle \cos \theta_{\text{il}} \rangle$: values of $\cos \theta_n$ for DTA are consistently larger than those for DS, and the differences between the two surfactants tend to disappear as one considers bonds closer to the chain ends. Finally, concerning the conformational analysis of the hydrocarbon chains, for the DS case, the increase in the end-to-end length (see the last column of Table 1) indicates a reduction in the number of *gauche* bonds with respect to the infinitely dilute case. Note that this behavior is accordant with the observed ratios between the signals from methylene and methyl symmetric stretching modes, obtained from sum frequency spectroscopy experiments.¹⁹

We now turn to the analysis of the surfactant structures. In all cases investigated, systems that started with randomly distributed headgroups rapidly developed the spontaneous formation of spatial domains of clustered surfactants. This phenomenon is, in principle, akin to the one we have already observed at interfaces with adsorbed sodium dodecylsulfate, at similar submonolayer coverages.³⁹ However, in this case, due to the strong Coulomb coupling between oppositely charged headgroups, the tendency for clustering is considerably enhanced. The prevailing overall surfactant structures can be pictured as a single asymmetric, stringlike domain, spanning over length scales comparable to the size of the simulation box. Figure 8 shows a snapshot for one of such configurations.

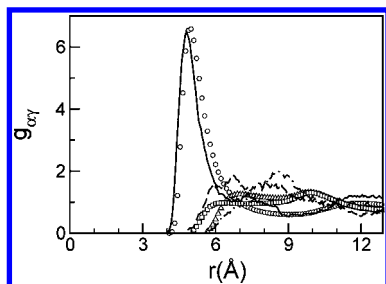


Figure 9. Two-dimensional pair correlation for adsorbed headgroups: S–N (solid line); S–S (dashed line); N–N (dot–dashed line). Also shown are results from a 2-D charged Lennard–Jones fluid (see text): S–N (circles); S–S (squares); N–N (triangles).

Given this scenario, one can speculate to what extent the characteristics of the observed structures are connected to the strong Coulomb coupling between headgroups. To shed light into this hypothesis, in the right panel of Figure 8, we show the same configuration as that of the left-hand side, after having eliminated the hydrophobic tails. This allowed us to unveil the layout of the adsorbed charged groups, represented here by S and N sites. The overall picture looks very much like a two-dimensional (2-D), “percolative” array. To quantify the observed structures more precisely, we computed spatial correlations between adsorbed headgroups. In this case, it was useful to analyze two-dimensional pair correlations of the following type:

$$g_{\alpha\gamma}(r) = \frac{A}{2\pi r N_s^\alpha N_s^\gamma} \left\langle \sum_{i,j} \delta(|\mathbf{r}_i^\alpha - \mathbf{r}_j^\gamma| - r) \right\rangle \quad (7)$$

where \mathbf{r}_i^α refers to the two-dimensional coordinate of site α ($\alpha = \text{N, S}$) in the i th surfactant molecule, i.e., $\mathbf{r}_i^\alpha = (x_i^\alpha, y_i^\alpha)$, and N_s^α represents the number of adsorbed sites α . Results are displayed in Figure 9: As expected, correlations between oppositely charged headgroups are dominant, with a main peak at $r = 4.8 \text{ \AA}$, including ~ 2 headgroups. Note that the position of this peak practically coincides with the global minimum of $W(r)$ for the surfactant pair and is also comparable to the rough estimate obtained from experiments at the critical micellar concentration, $\rho_s^{-1/2} \sim 5.5 \text{ \AA}$.¹⁸ N–N and S–S correlations show featureless profiles, although it is clear that the effective distance of closest approach between similar headgroups is smaller for DS than for DTA. This fact that is also accordant with the experimental values of saturated monolayer surface densities of sodium dodecylsulfate $\rho_s^{-1/2} \sim 6.7 \text{ \AA}$ ⁴⁰ and dodecyltrimethylammonium bromide, $\rho_s^{-1/2} \sim 6.9 \text{ \AA}$.⁴¹

We finally investigated whether the essential features described above could be captured by a much more simplified model, involving a handful of charged spheres. The first step in this direction was to adopt a model Hamiltonian; the simplest choice was the consideration of a mixture of charged Lennard–Jones spheres, constrained to move on a plane. The model was built as follows: (i) In this crudest level of approximation, all effects coming from the hydrophobic tails were disregarded. (ii) The presence of the solvent was incorporated by an appropriate choice of energy and length parameters. (iii) Lennard–Jones length parameters were chosen according to the following criteria: For N–S, we took the value of the minimum of the potential of mean forces of Figure 5. For N–N and S–S, we adopted typical values of the hydrated SO_4^{2-} and $\text{N}(\text{CH}_3)_3^+$ species ($\sigma_{\text{SS}} = 5.26 \text{ \AA}$; $\sigma_{\text{NN}} = 5.94 \text{ \AA}$).⁴² The choice of hydrated species accounts for the fact that the distances of closest approach for equally charged species at the interface may be affected by the presence of tightly bound water in the close

vicinity of the headgroups. In the left-hand side of Figure 8, we have also highlighted those water molecules in the vicinity of the headgroups. It is clear that the connectivity pattern of the cluster can be thought of as a sequence of zigzagged N–S contact ion pairs, with alternate N–N and S–S second nearest neighbor pairs, wedged by interfacial water molecules. (iv) As per the Lennard–Jones energy parameters, one can anticipate that the overall structures will be weakly affected by the choice of these parameters and, in all cases, they were set to a value comparable to thermal energies $\epsilon/k_B = 300 \text{ K}$. (v) Finally, following the spirit of the restricted primitive model for bulk ionic solutions,⁴³ Coulomb interactions were screened via an effective dielectric constant ϵ_{int} for the interfacial environment. An a priori estimation for this value is not straightforward; several attempts have been made in the past to provide estimates of this value. In most cases, however, the value of ϵ_{int} was considered as an adjustable parameter. In this particular case, the interfacial dielectric constant was set to $\epsilon_{\text{int}} = 20$, a value that is comparable to that adopted in previous studies.⁴⁴

For the sake of direct comparison, results from this simplified Coulomb model are also included in Figure 9. One observes that, despite the drastic approximations involved, the profiles obtained from this two-dimensional model still retain a great deal of the characteristics of the spatial correlations between the adsorbed headgroups. This observation would suggest that Coulomb forces between headgroups play a key role in determining the observed structures of spatial domains in this coverage regime.

V. Concluding Remarks

The molecular dynamics experiments described in this paper provide new features related to the solvation of complex amphiphilic structures adsorbed at water/air interfaces. Perhaps the most important conclusion that can be drawn from our results is the close correspondence that we have observed between surface states of catanionic surfactants and the solvation of simple ionic species in aqueous solutions. In fact, one can make reasonable interpretations of many phenomena presented in this work by invoking arguments derived from classical theories of aqueous electrolytes; most notably, those related to the concept of ionic association.

Our results clearly demonstrate that the stable solvation structure of symmetric catanionic surfactants at infinite dilution corresponds to contact-head-ion-pairs. Moreover, the interactions between the hydrophobic tails and, more importantly, the reactive field exerted by the interface are strong enough so as to considerably reduce the Coulomb attraction between the charged headgroups. In fact, an estimate based on a simple geometrical parameter as a reaction coordinate, suggests that the activation free energy for dissociation should be comparable to typical thermal energies. The magnitude of this barrier, however, clashes with the observed dissociation time scales that we monitored along fairly long trajectories, indicating that kinetic predictions based on TST are inadequate. This discrepancy, in turn, would also reveal the complexity of the reactive path followed by the system along the multidimensional potential energy surface that dictates the dynamics of the dissociation process at the aqueous interface.

At moderate surface concentrations, solvation clearly modifies tilts and local orientations of the surfactant tails. Besides the usual tendency toward a more perpendicular alignment, we stress the disappearance of the dual perpendicular/parallel accommodation of DS found at infinite dilutions. Under these circumstances, the combination of the strong Coulomb coupling

between headgroups along with the still relatively low surface coverage promotes large surfactant concentration fluctuations at minimal entropic costs. These fluctuations give rise to energetically stable surfactant domains, exhibiting asymmetric shapes and, in many cases, percolative structures. In passing, it is important to keep in mind that, given the limited number of particles considered in this study, we do not discard the possibility that these structural characteristics may be affected by finite size effects. Leaving aside these technical problems, we still believe that the results from our simulations remain physically sound. To bring support to this assertion, we have verified that the most important characteristics of the surfactant domains can be captured by considering a very much simplified, effective Hamiltonian, involving a mixture of asymmetric charged spheres constrained to move on a plane.

There are still many open questions that will require additional research to gain a more comprehensive understanding of the nature of adsorbed catanionic monolayers. We can think of, at least, two particularly relevant problems that we plan to tackle in a near future: (i) As we mentioned above, it would be important to corroborate to what extent the observed two-dimensional surfactant structures might be modified if one enlarges the simulated systems. The analysis of larger systems would also confirm the characteristics of the phase equilibria invoked to rationalize nonlinear spectroscopy results.¹⁹ (ii) The extension of the present experiments within the full monolayer coverage regime is certainly worth pursuing. However, given that the lateral diffusion for simpler ionic surfactants at full coverages is typically 1 order of magnitude slower than the one observed for the aqueous substrate,²⁵ we can anticipate that proper sampling of all relevant local concentration fluctuations at the interface will require simulation runs considerably longer than those presented here.

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